EXPERIMENTAL PHYSICAL CHEMISTRY

Experimental
Physical Chemistry

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Third Edition
THIRD IMPRESSION

EXPERIMENTAL PHYSICAL CHEMISTRY

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PREFACE TO THE THIRD EDITION

This revision introduces many new experiments and revises others in an attempt to keep abreast of the rapid developments in physical chemistry. Some of the former experiments have been eliminated or expanded because they have found their way into earlier courses and are already known to students, who each year come better prepared for the study of physical chemistry.

A certain amount of elasticity is needed in the amount of laboratory work covered in a single experiment, depending on the time and equipment that are available and on the experience and capacity of the student. When an experiment is too short, the student will find interesting things to do under "Suggestions for Further Work"; when it is too long, the instructor will select parts of the "Procedure" which may be omitted. Several of the procedures have been expanded and the directions made more specific without sacrificing the development of self-reliance on the part of the student, which has always been one of the aims of this book.

The discussion of more advanced apparatus and techniques in Parts II and III is relatively less complete than before because so much excellent new material is being published and because more specialized reference books for the laboratory, particularly in organic chemistry and physics, are now available.

The authors are glad to acknowledge the many helpful suggestions that have come from Professor W. E. Roseveare, Dr. T. F. Anderson, Mr. Milton Goff, Mr. A. E. Edwards, Mr. Lee K. Henke, and many students and others.

They are indebted to Mr. Henry H. Schmalz, a student in the :, for the helpful new drawings.

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MADISON, WIS.,
July, 1941.

PREFACE TO THE FIRST EDITION

To illustrate the principles of physical chemistry, to train in careful experimentation, to develop familiarity with apparatus, to encourage ability in research—these are the purposes of this book.

The imperative is not used. Procedures are described but orders are not given. The student must study the experiment first and then set his own pace—a method which develops both his power and his interest.

Some of the experiments are new, some are based on researches described in the literature, and some are classical. Considerable choice is available and selection will be made on the basis of available apparatus and on the maturity and ultimate aims of the student.

The second part of the book describes apparatus and technique, particularly for more advanced work. It is designed not only to encourage students to undertake special work but to aid them in later years in the solution of practical problems. No claim whatsoever is made for completeness. In their selection of material the authors have been guided simply by their own experience.

In a large class, several different experiments must go on at the same time and many of them are necessarily performed before the material has been studied in class. For this reason, space is devoted at the beginning of each experiment to a brief statement of the theory involved.

The experiments are based on the experience of several years at the University of Wisconsin where thirty to thirty-five experiments are assigned during the year and an average of eight hours of laboratory time is allowed for each. Many of the experiments can be done in less time, and the student is urged to follow the suggestions given for further work. Particular encouragement is given for original work.

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MADISON, WIS.,
October, 1929.

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COMMENTS CONCERNING LABORATORY WORK

In general, every determination should be made in duplicate. One cannot rely too heavily on a single experiment, because it may contain an accidental mistake. Close checks do not necessarily guarantee accuracy, since the same error may be repeated, but if duplicate results do not check the experiment is obviously unsatisfactory. Check experiments are more valuable if they are carried out under widely different conditions.

Any experiment worth doing is worth a careful report. Accurate reports should become a habit. They should include a discussion of the theory, the derivation of all formulas, and the original data. They should be neat, systematic, and unbiased. A true scientist cannot let his data be influenced by a preconceived hypothesis, nor must a student be influenced in his calculations by a knowledge of the correct result.

If the data are suitable for graphing, they are plotted neatly on coordinate paper and a curve is drawn, using a ruling pen and India ink.

The accuracy of the results should be critically evaluated, and, whenever possible, the averaged value of the measurements compared with the accepted value in the tables mentioned below. The percentage error is then calculated whenever justifiable.

The International Critical Tables (McGraw-Hill Book Company, Inc., New York, 1928–1933) contain the best constants, critically evaluated by experts. Landolt-Börnstein's "Physikalisch-Chemische Tabellen" contain a great number of experimental constants but they have not been critically evaluated. The "Tables Annuelles" published in English by the McGraw-Hill Book Company, Inc., are valuable also. For useful tables, Van Nostrand's "Chemical Annual," the "Handbook of Physics and Chemistry" published by the Chemical Rubber Company, and Lange's "Handbook of Chemistry" published by Handbook Publishers, Inc. Sandusky, Ohio, are recommended.

For advanced technique in physical chemistry the worker is referred to Parts II and III of this book or to the original literature or to the following treatises: Reilly, Rae, and Wheeler, "Physico-chemical Methods" (D. Van Nostrand Company, Inc., New York, 1940); Strong, "Procedures in Experimental Physics" (Prentice-Hall, Inc., New York, 1939); Morton, "Laboratory Technique in Organic Chemistry" (McGraw-Hill Book Company, Inc., New York, 1938).

EXPERIMENT NUMBERS

To facilitate the use of the new book with laboratory schedules based on the second edition, the corresponding experiment numbers of the two editions are listed here. Old experiments which have been changed considerably are given in italics. Minor changes have been made in many of the experiments.

Second edition	Third edition	Second edition	Third edition	Second edition	Third edition	Second edition	Third edition
1	1	18	20	39	42	59	..
2	2	19	21	40	43	60	58
3	..	20	22	41	44	..	59
4	3	21	23	42	45	..	60
..	4	22	*24*	43	46	..	61
5	5	23	*25*	44	..	61	..
6	6	24	26	45	47	62	..
7	..	25	27	46	..	63	..
..	7	..	28	47	54	64	62
8	8	26	*29*	48	50	65	63
9	9	27	*30*	57	..	66	..
10	10	28	35	49	*48*	67	64
11	11	29	36	50	..	..	65
12	12	30	37	51	49	68	*66*
..	13	31	33	52	*51*	69	69
..	14	32	31	53	..	70	*67*
13	*15*	33	32	54	52	..	68
14	16	34	34	55	53	71	70
15	17	35	38	56	*57*	..	71
..	18	36	39	..	55	..	72
16	..	37	*40*	..	56		
17	19	38	41	58	..		

The following more or less classical experiments are recommended to cover important principles or techniques when only a limited time is available for laboratory work: 2, 5, 10, 15 or 16, 22, 25, 31 or 32, 38 or 39, 44, 49, 53, 67 or 69.

The following experiments may be done without any special equipment beyond ordinary glassware, balance, thermometer, etc.: 2, 3, 5, 6A, 7, 8, 16, 19, 20, 21, 23, 25, 26, 27, 29, 30, 32, 33, 34, 35, 37, 38, 40, 41, 42, 43.

The following experiments may be of special interest to students of the biological sciences: 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 22, 25, 26, 29, 39, 43, 49, 50, 51, 61, 65, 66, 67, 71.

PART I
LABORATORY EXPERIMENTS

CHAPTER I

GASES

1. Gas Density

This experiment illustrates the simplest and most direct method for determining molecular weights. It provides experience in the weighing of gases. The method to be used was devised by Regnault.

Theory.—According to Avogadro's law, equal volumes of gases at the same pressure and temperature contain the same number of molecules, and their weights are, therefore, proportional to the molecular weights. Oxygen is taken as the standard, 1 molecule (O_2) having a weight of 32 units. Careful experiments have shown that 32 g of oxygen at 0°C. and 760 mm pressure occupies a volume of 22,412 ml (after allowing for the deviations from a perfect gas). A gram molecule (mole) of any substance contains 6.02×10^{23} individual molecules. Within the limits of the simple gas laws, then, the weight in grams of 22,412 ml of any gas measured at 0° and 760 mm is equal to its molecular weight. The value 22,400 ml is sufficiently exact for ordinary purposes.

In the laboratory, it is more convenient to work with a smaller volume of gas at room temperature and at barometric pressure. From the experimentally determined weight of a volume of gas under a certain temperature and pressure, the weight of 22,400 ml of the gas at 0°C. and 760 mm can be calculated.

Apparatus.— A 200-ml thin-walled bulb provided with a small stopcock; counterpoise; thermostat; balance; vacuum pump; carbon dioxide; hydrogen, and other gases.

Procedure.—Air and other gases are weighed in the glass bulb shown in Fig. 1. The evacuated bulb is first weighed; the difference in weights gives the weight of the gas. The volume is determined by weighing the bulb when filled with water.

In weighing large glass vessels, it is necessary to maintain uniform conditions. The bulb is wiped with a clean, damp cloth and allowed to stand in the balance for 5 or 10 min. to come to constant weight. A counterpoise, consisting of a closed glass bulb of practically the same volume, is used on the opposite balance pan to minimize errors due to

adsorption of moisture and changes in buoyancy of the air due to barometric fluctuations.

The assembled apparatus is shown in Fig. 1. The gases are weighed in the glass bulb having a stopcock shown at *A*. The pressure is read to a fraction of a millimeter on the closed-end manometer shown at *B*. The temperature is controlled by the water bath *C* which is
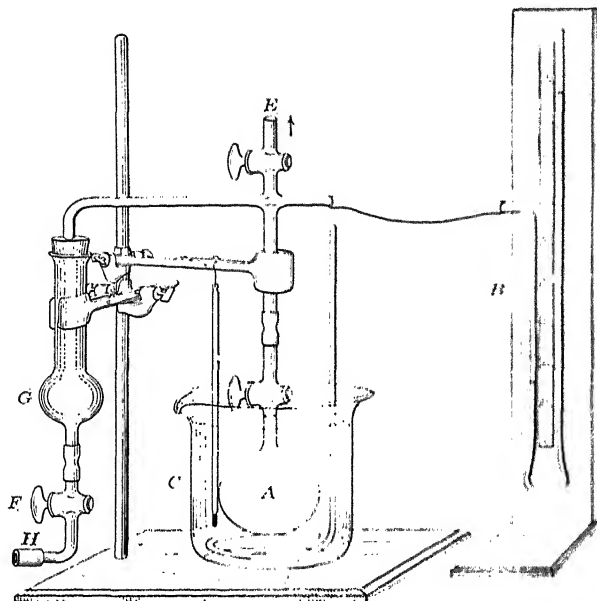
Fig. 1.— Apparatus for determining the density of a gas by

close to room temperature. The bulb *A* is immersed nearly but not quite to the stopcock because it is difficult to remove drops of w from the stopcock. The water is stirred by hand and should be stant within a few tenths of a degree for a few minutes before the cock is closed.

The bulb is first evacuated to 0.1 mm or less with a motor-driven oil pump (page 312), while stopcock *E* is open and stopcock *F* is closed. Any visible moisture in the bulb must be removed by connecting to a water aspirator and setting in warm water. Water and other must not be allowed to get into the oil of the vacuum pump. F

tion is not satisfactory unless the two mercury surfaces are at exactly the same level and remain so when stopcock E is closed. Leaks at the rubber connections may be stopped by substituting new gum rubber or by winding a tightly stretched rubber band around the connection and wrapping with electrician's tape or surgeon's plaster. Leaks at the stopcocks may be stopped with more stopcock grease, or a new stopcock with better ground surfaces may be substituted.

The stopcock at A is closed, and air is admitted to the connecting tubes through the drying tube G by opening the stopcock F. The bulb A is removed from the rubber connecting tube, wiped with a clean, damp, lintless cloth, and allowed to hang in the balance for 5 or 10 min. to come to constant weight. A counterpoise consisting of a closed glass bulb of practically the same volume (and wiped in the same way) is used on the opposite pan.

The bulb is replaced in the apparatus and subjected to a second evacuation, after which it is weighed again. If the two weights do not check, the process is repeated until they do check.

After determining the weight of the evacuated bulb, the weight of the bulb when filled with dry air is determined next. The bulb is replaced in the water bath, evacuated while stopcock E is open and F is closed. Then E is closed and F is opened. This procedure is followed by a second evacuation and a second filling with air. The water bath is held at constant temperature for 3 or 4 min., and the temperature and manometer readings are taken as the stopcock on the bulb A is closed. After wiping with a damp cloth and waiting for uniform conditions in the balance case, the bulb of air is weighed.

The bulb is replaced for another evacuation and a second filling with air and weighed again, after recording the temperature and pressure at which the stopcock on the bulb was closed.

Stopcock F is next removed, and a tank of carbon dioxide or other gas, with its valve closed, is connected. A loosely fitting rubber tube H is used to connect the tank to the drying tube, so that it will blow off as a safety valve in case the pressure is carelessly allowed to become appreciably higher than the atmospheric pressure as registered on the manometer. The bulb A is inserted, its stopcock is opened, stopcock E is opened, and the whole apparatus is evacuated. Stopcock E is then closed, and the manometer reading should remain constant, showing the absence of leaks. Then the valve on the gas tank is opened cautiously and slowly until the manometer reads about atmospheric pressure. The tank valve is closed, E is opened, and the whole system is evacuated a second time to remove further all traces of air or

other gas formerly contained in the bulb.   It is again fille
with carbon dioxide, the measured temperature and pressure are
recorded, and the bulb is weighed.

The weight of carbon dioxide is determined in the same manner at
about three-fourths and again at about half an atmosphere.   It is
essential in this work that there be no leaks.

If time permits, the density of illuminating gas or of some unknown
gas or mixture of gases may be determined.

When the gases have been weighed, the bulb is evacuated and
opened with the tube end under recently boiled distilled water at a
definite temperature.   If there is an air bubble, the bulb is inverted
and water introduced with a fine tube drawn down so as to pass
through the bore of the stopcock.   Any moisture above the stopcock is
carefully wiped out.   The filled bulb is wiped and weighed.   The
bulb is drained and dried with the aspirator before putting away.

Calculations.— If the counterpoise has practically the same volume
as the bulb, it is unnecessary to make a correction for the buoyancy of
the air.   If a counterpoise is not used, it must be remembered that each
cubic centimeter of air displaced gives a buoyant effect amounting to
1.2 mg and that this weight must be added to the observed weight.
This correction is reduced by 12 per cent, however, because the brass
weights having a density of 8.5 give a buoyant effect in the opposite
direction.

The volume v of the bulb in cubic centimeters is calculated by
dividing the weight of water by the density of water at the temperature
of filling.   At 25° the density is 0.99704.

The weight of the gas g is obtained by subtracting the weight of the
dry evacuated bulb from that of the bulb when filled with the gas.

The pressure p is read from a barometer, corrected to 0° (page 451),
and converted to atmospheres.

The absolute temperature T is the temperature of the thermostat
$(t° + 273.1°)$.

The molecular weight M of the gas is calculated from the equation

$$pv = \frac{g}{M} RT$$

where R is 82.06 ml-atm. deg.$^{-1}$ mole.$^{-1}$

The average "molecular weight" of air is calculated and compared
with the value calculated from the known composition of the air.

The measurements at different pressures constitute a check on
Boyle's law.   If carbon dioxide were a perfect gas, the molecular
weight would be the same at all pressures, but actually it decreases at

the lower pressures. In fact, one of the most accurate ways of determining the true molecular weight of a gas is to plot the molecular weight obtained at different pressures and extrapolate the line to zero pressure.

Practical Applications.—The formula of a chemical compound may be calculated from the molecular weight, together with the atomic weights, and the percentage composition found by chemical analysis.

The chemical equilibrium between different gases may often be calculated from the density of the equilibrium mixture of gases.

Suggestions for Further Work.—The accurate determination of the molecular weight of hydrogen gas by this method constitutes a real test of a student's care and skill.

The molecular weights of other gases may be determined. Small tanks of methane, ethylene, nitrous oxide, and other gases can be purchased.

The percentage composition of a mixture of two gases such as oxygen and carbon dioxide may be determined from the density of the mixture.

More exact values of the molecular weights may be calculated with equations of state such as Berthelot's, van der Waals', or Beattie and Bridgman's.

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2. Vapor Density

This experiment illustrates a practical method for determining the molecular weight of a volatile material. It provides excellent practice in setting up simple physical-chemical apparatus.

Theory.—The density of a vapor is more easily determined than the density of a gas because the substance may be weighed accurately when it is condensed to a liquid at room temperature.

There are several ways in which the necessary determinations of pressure, volume, and weight may be made (pages 303 and 304).

The method of Victor Meyer is the simplest and the one most frequently used. The volume of air displaced by the vaporization of a known weight of liquid is carefully measured.

Apparatus.—Modified Victor Meyer apparatus; gas burette and leveling bulb; 1° thermometer; barometer; glass bulblets; carbon tetrachloride, benzene, acetone, or chloroform.

Procedure.—A modified form of Victor Meyer apparatus is shown in Fig. 2. The outer jacket *A* is made from a pyrex tube (5 by 40 cm).

A rubber stopper holds the inner vaporizer tube in the outer jacket, through which live steam is passed. At the bottom of the jacket a small tube is sealed, through which the excess steam and condensed water are led to the sink. A discarded ether can C, provided with a safety tube, serves as a steam generator. The vaporizer tube is
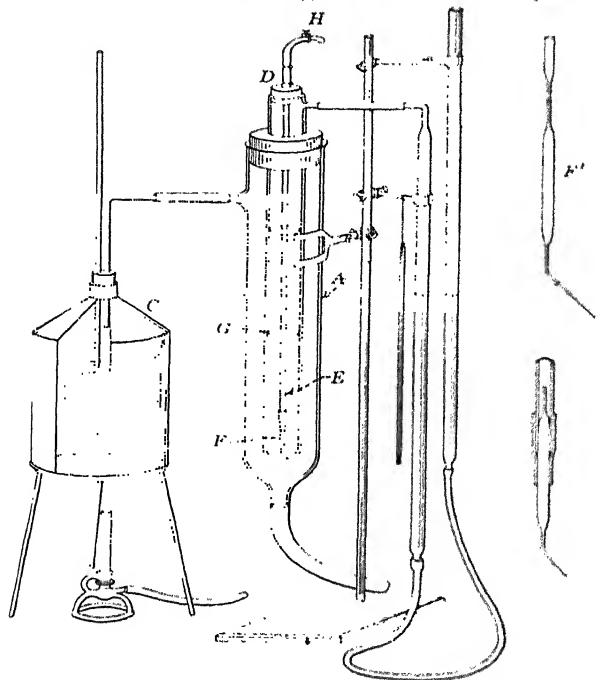
а. 2.—Modified Victor Meyer apparatus for vapor density.

provided with a rubber stopper containing a glass tube and a section of heavy rubber tubing D through which passes a long brass (or glass) tube. The purpose of this flexible joint is to permit the central tube E to be pushed down slightly, so as to break off the capillary end of the bulblet F that contains the liquid, after which the tube springs back into its original position. This central tube carries three or four disks G nearly filling the cross section of the vaporizer tube, the purpose being to reduce the rate of diffusion of the vapor produced when the bulblet is broken. The disks are cut from thin metal and

with central holes so that they can slip over the supporting tube. They are soldered in position or supported by rings of wire twisted around the tube. Mica disks and a glass tube are used for corrosive gases.

The bulblet containing the liquid to be vaporized is inserted in the bottom of the tube E and held in position with two semicircular extensions of sheet copper soldered to the tube. The jaws are sprung inward. The rubber tubing at the top of the central tube is provided with a screw cock H. The gas burette of 50 ml capacity and leveling tube contain enough water to bring the level to the zero mark on the burette when the leveling tube is raised.

The little bulblet is made by drawing out 4-mm glass tubing to form a little pipette with a body about 4 cm long and a slender capillary at each end, the lower capillary being bent as indicated in the enlarged view at F'. It is then weighed on an analytical balance. The liquid to be used is drawn into the weighed pipette from a small dish or watch glass by suction, a small-diameter rubber tube or a glass tube with a short rubber connection being used. Enough liquid is drawn up to give about 25 to 30 ml of vapor (roughly 0.1 ml of liquid), and the little tube should be of such length that it is filled approximately three-fourths full, leaving room for expansion of the liquid. The upper capillary is then sealed off with a micro gas flame issuing from a capillary tube of pyrex (or quartz). The little tube is next inverted so that the liquid runs down, out of the bent capillary, and it is sealed off beyond the bend at the place indicated by the line. The bulblet with its liquid and the two sealed-off ends are then weighed again to obtain the weight of the liquid. Any liquid remaining in these sealed-off ends must be removed before weighing.

The vaporizer tube must be freed from any vapor it may contain. This is accomplished by drawing a gentle current of air through the tube E after steam has been passing through the jacket for some minutes. A water aspirator is attached at H. The apparatus is assembled with the sealed bulblet as shown and, after steam has passed through the jacket for at least 10 min., is tested for leaks and for thermal equilibrium by closing the screw cock H and lowering the leveling tube. If the liquid in the burette does not continue to fall after the leveling bulb is held in a definite position, the apparatus is tight and in thermal equilibrium. The leveling tube is then raised until the liquids in the two tubes are exactly level, and the reading of the burette is recorded.

The central tube is now pushed down sufficiently to lower capillary tip of the bulblet, whereupon

quickly. As the vaporization takes place, the leveling tube is lowered so as to maintain nearly equal pressure inside and outside the apparatus, to prevent possible leakage. When the hot air, displaced into the gas burette, cools, a slight contraction may be noted. When the level of the liquid in the burette ceases to change position, the levels of the liquid are carefully adjusted to exactly the same height and the final reading of the volume is made. After standing for some time, the volume of the measured air decreases, because of diffusion of the vapor from the vaporizer into the cooler parts of the apparatus where it condenses. Obviously, the final reading must be taken before this occurs. The temperature of the displaced air, thus measured, is taken from a thermometer hanging by the burette. For more precise work, the measuring tube may be jacketed with a concentric tube containing water and a thermometer.

Careful planning is essential in all experimental work; *e.g.*, in this experiment, while the bulb is coming to temperature, a second bulblet may be prepared and weighed.

Carbon tetrachloride, benzene, or any low-boiling liquid may be used. The material must be pure. Two or more determinations are made until satisfactory checks are obtained. After each determination the vapor is removed before a second experiment is started, for an excessive volume of vapor leads to diffusion and condensation in the connecting tube.

The molecular weights of one or more compounds is to be determined, duplicate determinations being made as usual. The apparatus should not be disturbed until the calculations have been made and the results checked.

Calculations.—The pressure is read from the barometer, corrected to 0°C. with tables (page 451). The correction amounts to 2 or 3 mm. The vapor pressure of water (page 452) at the temperature of the burette must be subtracted from the barometer reading because part of the volume of the gas registered in the burette is due to evaporation of water into the dry air expelled from the vaporizing jacket.

The molecular weight M of the vapor is calculated from the familiar equation

where p = the pressure in atmospheres.
v = the volume in milliliters of the displaced air.
T = the absolute temperature at which it is meas
g = the weight of the liquid taken.
R = the gas constant, 82.06 ml-atm deg.

The averaged results are compared with the accepted values and the percentage error is calculated. A reasonable error involved in each reading is estimated, the various causes of error are enumerated, and the accuracy attainable is discussed critically.

Practical Applications.—The determination of the molecular weight is useful in identifying a chemical compound and in establishing its formula.

When gases dissociate on heating, the equilibrium may be determined quantitatively through density measurements.

Suggestions for Further Work.—The density of several organic or inorganic vapors may be measured. For substances having boiling points above 80°, some liquid boiling higher than water must be used to generate vapor for the jacket. The jacket should be at a temperature at least 20° above the boiling point of the substance whose vapor density is being determined, because of the failure of the gas laws to apply to vapors that are near the condensation point.

Better results are obtained by using van der Waals' equation or Berthelot's equation. A convenient form of the latter is

$$M = w \frac{RT}{PV} \qquad \frac{9}{128} \frac{P}{P_c} \frac{T_c}{T_s} \left(1 - 6 \frac{T_c^2}{T_s^2} \right) \Bigg]$$

where P_c and T_c are the critical pressure and temperature of the compound used and T_s is the temperature of the jacket (373°).

The methods of Dumas, Hofmann, or Lumsden may be used for the determinations.

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3. Effusion of Gases

MOLECULAR WEIGHTS AND MOLECULAR DIAMETERS

This experiment illustrates the determination of molecular weights and molecular diameters by effusion. The measurements are so simple that several determinations can be made and treated by the rules for computing errors.

Theory.—The fundamental formula describing the velocity of gas molecules is given in equation (1)

$$pv = RT =$$

where R = the gas constant in ergs per degree.

T = the absolute temperature.

p and v = the pressure and volume of the gas.

m = the weight of a single molecule.

n = the number of molecules.

u = the velocity of a molecule in centimeters per second.

Since the average kinetic energy of the molecules is the same at a given temperature, equation (2) may be deduced from equation (1) for very low pressures where the mean free path is smaller than the diameter of the hole.

where m_1 and u_1 apply to one gas, and m_2 and u_2 to a second at the same temperature and pressure.

If different gases are allowed to escape through a small hole under the same temperature and pressure, the number of molecules passing through will depend only upon the velocities with which the molecules travel, for the number traveling will be the same for the different gases at the same temperature and pressure. Since the times t_1 and t_2 required are inversely proportional to the velocity, it follows that

If the molecular weight of one gas is known, and the times of effusion under the same conditions are known for the two gases, the molecular weight of the second may then be calculated. Although this formula is valid only for very low pressures it may be used for approximate comparisons between gases of similar heat capacity.

These considerations apply to effusion of gas through a pinhole in a very thin piece of foil where the walls play a negligible role. When the molecules stream through a long capillary tube, on the other hand, the wall greatly affects their movement, and the viscosity of the gas rather than the molecular weight is involved. Under these conditions the molecules in the center move fastest and transfer their velocity by collision to molecules nearer the sides of the capillary. These in turn transfer their energy to the wall and slow down the stream, giving rise to the phenomenon of viscosity. The rate of escape will depend not only on the velocity of the molecules but also on the resistance to flow caused by collision with the walls and with each other. The viscosity depends on the frequency of collision, and this in turn is a function of the diameter of the molecule.

The following relation can be derived with the help of the kinetic theory of gases. When two different gases at the same temperature and initial pressure are allowed to stream through a capillary tube,

$$\sigma_2 = \sigma_1 \sqrt[4]{\frac{t_1^2 M_2}{t_2^2 M_1}} \tag{4}$$

where σ, t, and M refer to the molecular diameter, time, and weight, respectively.

The number of collisions z per second in a milliliter is calculated with the help of the equation

$$z = \frac{\sqrt{RT}}{} \tag{5}$$
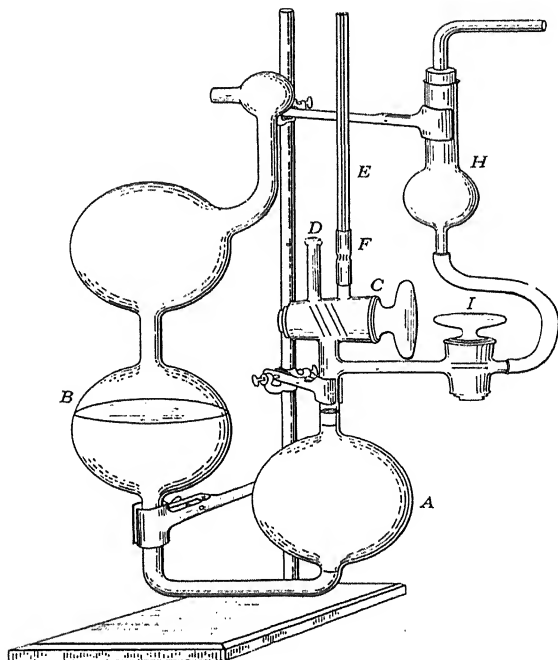
FIG. 3.—Apparatus for measuring the rate of effusion of a gas through a small hole and through a capillary.

where n is the number of molecules in a milliliter, M is the molecular weight, and R is the gas constant in ergs per degree.

Apparatus.—Effusion apparatus; purified mercury; stop watch; oxygen, carbon dioxide, hydrogen, calcium chloride drying tube.

Procedure.—The effusion apparatus shown in Fig. 3 consists of two bulbs of approximately 50 ml capacity partly filled with mercury. The gas is forced into reservoir A, driving the mercury back into the higher bulb B.

The upper bulb is slightly larger than the lower one so that the mercury level will go below the lower mark when filling with gas and above the upper mark when forcing the gas out. By turning the stopcock C the gas can be made to leak out (a) either through the hole in the disk at D, giving a measure of the molecular weights, or (b) through the long capillary tube E, giving a measure of the molecular diameter. The disk is prepared from a piece of very thin platinum foil perforated with a sharpened needle point while lying on a piece of paper on a hard surface. It is attached with sealing wax. The capillary tube E, 25 cm or more in length and 0.2 mm in diameter, is inserted in the rubber connector at F only when in actual use; during the rest of the operations the tube ending at F is used as an exit for gases being rinsed out of the apparatus.

An oxygen tank provided with a needle valve is connected to the drying tube of fresh calcium chloride H with a rubber tube loosely attached so that it will blow off and act as a safety valve in case the pressure is carelessly allowed to become too high. The bubbling of gas through the mercury in bulb B will also relieve excess pressure if necessary. The capillary E is removed, the mercury is brought level as shown, and the needle valve is cautiously opened to give a slight stream of gas issuing at F. In this way, the gas formerly present is rinsed out.

Stopcock C is closed, and the gas slowly forces the mercury out of the bulb A. When the mercury reaches the lower mark, the needle valve is quickly closed. Stopcock I is closed, and the gas is allowed to escape once through F for additional rinsing. The process is repeated, this time the gas being allowed to escape through D. About 3 to 5 min. should be required for the escape of gas. The bulb is filled again with oxygen and allowed to leak through D. The stop watch is started when the mercury crosses the lower mark and stopped when it crosses the upper mark. Five successive determinations are made on the time required for the given volume of oxygen to leak out.

The capillary tube E is inserted at F, and five more determinations are made, the stopcock being turned for these determinations so that the gas escapes through the capillary tube.

The experiment is repeated with carbon dioxide from a tank, determining the time required for the effusion through the small hole in the foil, and effusion through the capillary. Five measurements are made on each.

The experiment is repeated with hydrogen from a tank.

The experiment is repeated with air, using compressed air as before.

Calculations.—The molecular weight of carbon dioxide and hydrogen and the average molecular weight of air are calculated with the help of equation (3), taking the molecular weight of oxygen as 32.00.

The corresponding molecular diameters are calculated by equation (4), taking the molecular diameter of oxygen as 3.4×10^{-8} cm.

The average value and the mean deviation from the average is calculated for each gas. The first determinations with a new gas may be affected by incomplete removal of the preceding gas. Accordingly, the first one or two determinations may be discarded if they are not in line with the later ones, but after an experimental result has been accepted all subsequent determinations of the same quantity must be included in the final results, unless some mistake or mishap occurred and was recorded in the notes previous to calculating the final result. If some results are obviously out of line with the others for no known reason, they must be recorded in the final results but they may be excluded from the average if the exclusion is specifically stated. Again a whole set of measurements may be discarded and a new set taken because the experimenter is unskilled or because the apparatus is not functioning properly. However, it is not permissible in science to select from a set of data only those readings which appear to give an expected answer or to be prejudiced in regard to any particular result. Moreover the expected answer may be wrong!

The number of collisions per milliliter between molecules is calculated for each gas by formula (5).

Practical Applications.—The method of effusion through a small hole furnishes a rapid means for determining molecular weights.

There are complications due to the different types of gas flow, but if these are overcome the method should be useful in quick analyses and identifications of organic compounds at low pressures, including solids and liquids which are only slightly volatile.[4]

The purity of gases and the analysis of mixtures may be determined by the rate of effusion through a small hole.[5,6]

The rate of effusion of a gas through a capillary is a standard and simple method for determining the viscosity of a gas. From a knowledge of the viscosity and the molecular diameter it is possible to calculate the collision frequency and mean free path of a gas, quantities that are useful in calculations of chemical kinetics and the prediction of reaction rates.[7]

Suggestions for Further Work.—The molecular weights and diameters of several gases may be determined, such, for example, as methane, ethylene, helium, ammonia, methyl chloride. Accurate results can not be expected.

The number of experimental determinations may be extended to 10 or 15 and the average error compared with that obtained with five determinations. The root-mean-square error and the probable error may be compared with the average error. The calculated molecular weights will not be identical with the sum of the atomic weights because formula (3) is valid only at very low pressures.

Mixtures of air and carbon dioxide or other gases may be analyzed by determining the average molecular weight. The reservoir may be filled with dried, exhaled air and an attempt made to determine the carbon dioxide content.

It is possible to operate the apparatus at reduced pressures by installing a proper connecting tube and partially evacuating both bulbs. With this attach-

ment, the molecular weights of some organic vapors such as acetone or methanol may be determined at room temperature.

It is instructive to calculate the number of collisions and the mean free path at a pressure of 1 atmosphere.

Other apparatus for measuring the viscosity of gases has been described by Rankine.[8]

The diameters of the molecules of several organic vapors of different types may be measured and compared with the molecular structure, and with interatomic distance measurements of crystal lattices. Interesting deductions have been made by Mack regarding the shapes of molecules.[9]

The frequency of collision on a flat, catalytic surface may be calculated from the data obtained here.

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4. Gas Density Balance

The difference between the density of a given gas or mixture of gases and the density of a standard gas is determined very accurately and conveniently by means of a density balance. The apparatus is used for the analysis of gas mixtures.

Theory.—The principle of Archimedes is used, according to which the upward force is equal to the weight of the gas displaced. A large glass bulb on a balance beam is counterpoised with a heavy weight to give a zero reading with air or oxygen at a given pressure. When the apparatus is filled with other gases, the pressure P is adjusted to give the same zero point, keeping the temperature constant. Knowing the density D of the standard gas, oxygen, the density of the second gas is given by the simple relation

$$\frac{D_{gas}}{D_{oxygen}} = \frac{P_{oxygen}}{P_{gas}}$$

Apparatus.—Gas density balance constructed of glass; manometer; barometer; thermostat; drying tube; water aspirator; carbon dioxide;

Procedure.—The gas density balance is shown in Fig. 4. It is not difficult to construct. The bulb is made from thin-walled pyrex glass, or preferably quartz, about 2.5 cm in diameter and 8 cm long. A 1-mm glass tube serves as the balance beam, and at the other end is a small bulb about 8 mm in diameter filled with a sufficient quantity of solder melted in to counterbalance the balloon in air. The bulb is sealed off and drawn out to a thin pointer. The beam is suspended at the center from a 2-cm crossarm by very fine, stiff wires leading off at the sides and anchored in the constricted side tubes. Silver chloride melted with a capillary gas flame is used for attaching the platinum wires to the enclosing glass tube and to sections of very fine tungsten wire holding the crossarm.
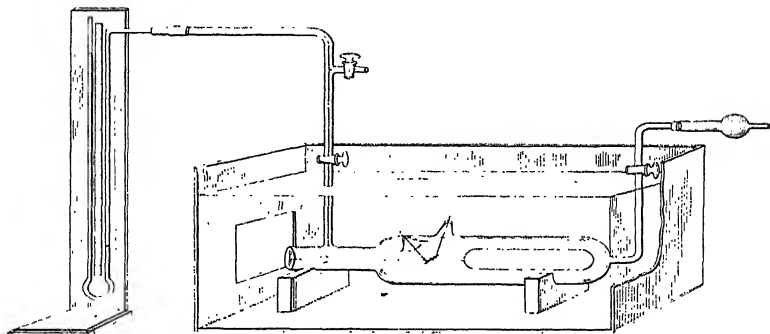
Fig. 4. Gas density balance.

The silver chloride is made by precipitation of silver nitrate with hydrochloric acid, washing thoroughly, melting, and casting into glass tubes. Before anchoring the suspension wires in the balance case, the beam is carefully balanced in air by melting on suitable weights of silver chloride.

The enclosing tube is made of 3.5-cm pyrex tubing 25 cm long, with connections as shown leading to purified air or gas, vacuum pump or aspirator, and manometer. One end is provided with a window; the other end is drawn down and connected to the tube after the balance beam has been inserted but before it has been suspended. A small scale is mounted in such a position that the pointer of the beam moves up and down immediately behind it.

The open-end mercury manometer gives the difference between the pressure in the balance and the atmospheric pressure, and barometer readings must be taken when the final manometer readings are taken.

The whole balance tube is set into a water thermostat with a glass window, and the end of the pointer is viewed with a lens through the transparent scale immediately in front of it.

Several readings are made on air that has passed through a tower of soda lime to remove water vapor and carbon dioxide. A position on the scale is chosen as a zero point, and the pressure necessary to bring the pointer to this zero is determined. In making fine adjustments of the pressure two stopcocks on the suction tube are convenient. By evacuating a small section of tubing, closing the farther stopcock, and opening the one nearest to the balance, the pressure may be reduced in small puffs.

The number of scale divisions in the balance corresponding to 1-mm difference on the manometer is determined so that the scale reading may be used for calculating the fractions of a millimeter pressure required for a zero setting.

Measurements are made first on dry air that has passed through the soda lime tube, and the pressure required to bring the pointer to zero is recorded.

The pressure reading for a zero balance on dried oxygen from a tank is determined next. When a new gas is introduced, it is essential to sweep out all the preceding gas. A second density reading is taken after further sweeping out with the new gas. If the two readings do not agree, the sweeping process is continued until two successive readings agree closely.

The relative density of carbon dioxide from a tank, dried with calcium chloride, is determined in a similar manner.

The apparatus is particularly well adapted to measuring the density of air mixed with small amounts of other gases. (For this purpose a greater accuracy can be obtained by filling the manometer with oil instead of mercury.) The carbon dioxide of the exhaled breath is determined by blowing the breath through a calcium chloride drying tube and a cotton packing into the balance.

In another determination the vapor pressure of carbon tetrachloride or other volatile liquid is determined by bubbling purified air through the liquid contained in a bottle in the thermostat, thence through glass wool to take out spray, and into the density balance.

Calculations.—The density of a gas is calculated by simple proportion from the known density of a standard gas and the pressure of the two gases which is required to bring the pointer to zero.

Over the moderate pressure range used here the density of a gas may be taken as directly proportional to the pressure, even though the gas is not quite a perfect gas. In the analysis of a mixture of gases the

density in grams per liter is determined with the balance, and the density of each pure gas at the same pressure is known. A formula is derived that will give the percentage composition corresponding to the observed density at the observed pressure. It is assumed that any interaction among the different gases leading to density changes is negligible in the experiments described here.

A critical evaluation of all the errors involved should be made, giving the percentage error that might result from errors in the readings of pressure and temperature and evaluating the effect of complications such as adsorption of gases on the balloon or impurities.

Practical Applications.—Exact measurements of the density of a gas are used for determining molecular weights, determining purity, and analyzing mixtures of

Suggestions for Further Work.—Among other gases whose density may be determined are illuminating gas and ethane, and other gases obtainable in tanks.

Vapor pressures may be determined by bubbling air through acetone, carbon tetrachloride, ethanol, or other liquids.

An experiment may be carried out on photosynthesis in which seedlings of wheat or any plants are grown in a bottle and the air surrounding them is swept into the balance through a calcium chloride tube. When the plants are exposed to bright light, carbon dioxide is consumed and oxygen in practically equivalent amount is evolved; while in the dark, oxygen is consumed and carbon dioxide is given off. These changes can be measured if there is a sufficiently large number of plants.

A liquid that has a fairly constant boiling point and is regarded as pure may nevertheless show large differences in vapor density, due to impurities, as the liquid is boiled away. For example, the thermostat may be set at 60° and a sample of acetone boiled through the balance. Unless the acetone is of exceptional purity, the first vapor will have a density appreciably less than that which comes from the last fraction distilled.

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CHAPTER II

LIQUIDS

5. Vapor Pressure

In this experiment the vapor pressure of a liquid is measured at several temperatures by reading the manometer and thermometer while the liquid is evaporating. Experience is gained in finding empirical equations to fit experimental data. The empirical constants are interpreted in terms of thermodynamical relations.

Theory.—Vapor pressure is defined as the pressure of the vapor that is in equilibrium with a liquid. Molecules are flying off continuously from the surface of the liquid because of their kinetic energy, and molecules are leaving the gas phase and going back into the liquid. When the rates of these two processes are equal, a "dynamic equilibrium" is said to exist. In a closed vessel, the equilibrium pressure is quickly established; but in an open vessel where the vapor can diffuse away, the liquid continues to evaporate indefinitely.

When the temperature is raised, the vapor pressure increases, because more molecules gain sufficient kinetic energy to break away from the surface of the liquid. When the vapor pressure becomes equal to the pressure of the gas space, the liquid boils. The temperature at which the vapor pressure reaches 760 mm of mercury is the *standard* boiling point.

An important relation, known as the Clausius-Clapeyron equation, connects the heats of vaporization of a liquid and the temperature coefficient of the vapor pressure. It may be expressed in several forms, the most convenient of which are

$$\frac{dP}{dT} \times \frac{1}{P} = \frac{d\ln P}{dT} = \frac{L}{RT^2} \tag{1}$$

or the integrated expression,

$$\log \frac{P_2}{P_1} = \frac{L}{2.303R} \frac{(T_2 - T_1)}{(T_2 \times T_1)} \tag{2}$$

In these equations P_2 and P_1 are the vapor pressures at the temperatures T_2 and T_1, L is the molar heat of vaporization, and R is the gas constant. L and R are expressed in the same units, usually calories.

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Apparatus.—Ramsay-Young apparatus; closed-end manometer; accurate thermometer; water aspirator; one liquid chosen from carbon tetrachloride, acetone, chloroform, benzene, alcohol, water, or other liquid boiling below 100°.

Procedure.—The apparatus is shown in Fig. 5. A long-necked 250-ml flask is provided with a two-hole rubber stopper holding an accurate thermometer and a small separatory funnel set so that the bent tip touches the thermometer. The thermometer bulb has one
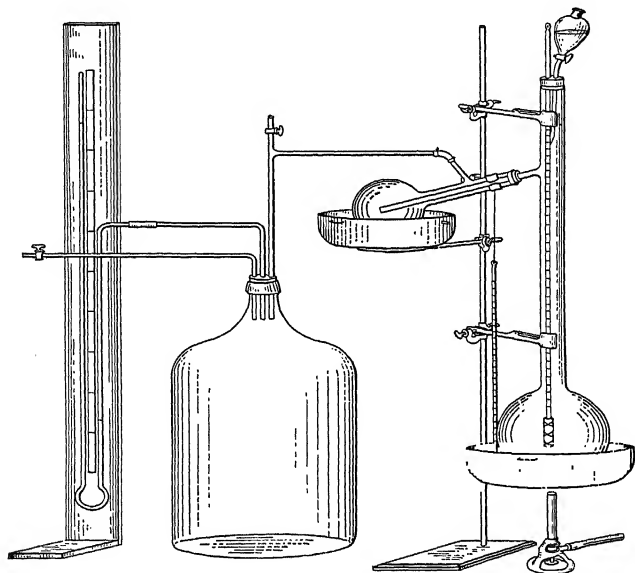
G. 5.—Ramsay-Young apparatus for measuring the vapor pressure of a liquid.

layer of muslin cloth wrapped around it and tied on with thread. The flask is evacuated with a water aspirator, connected through a 10-liter bottle which in turn connects with a closed-end manometer and a stopcock leading to the air. The large bottle is wrapped in ordinary fly screen (preferably copper) or placed in a wooden box to eliminate hazards of flying glass in case of breakage due to evacuation. A flask packed in ice condenses out the excess vapor distilled over.

The separatory funnel and cloth are rinsed with the liquid to be used in the experiment. If there is a *different* liquid in the flask from a previous experiment, it must be removed completely.

The stopper is set firmly in the flask, and the separatory funnel is closed and filled with the liquid. The system is exhausted, as far as possible, with the water aspirator, and the stopcock next to the pump is then closed. If the manometer rises, there is a leak in the system which must be stopped. New rubber stoppers may be necessary.

The stopcock of the separatory funnel is opened carefully, and liquid is allowed to run down the thermometer stem at such a rate that 4 or 5 drops of liquid fall off from the cloth wrapping of the thermometer bulb each minute. The water bath surrounding the flask is kept about 20° above the temperature registered by the thermometer bulb, and the flow of liquid is adjusted so that each drop evaporates before the next one falls.

The liquid on the cloth around the thermometer bulb is heated by condensation of vapor and by radiation from the flask and cooled by evaporation until a steady temperature is registered. This is the boiling temperature of the liquid at the pressure registered on the manometer, unaffected by superheating or slight impurities.

After the thermometer and manometer become steady, the two readings are recorded, and the stopcock of the reservoir bottle is opened to the air. The pressure is increased about 100 mm, and a second observation is made when equilibrium has been reached. The observations are continued less frequently at higher pressures, about five readings in all being taken before atmospheric pressure is reached.

By starting at atmospheric pressure and going to lower pressures, a different set of five observations is made.

Calculations.—Two graphs are plotted. In one, the vapor pressures are plotted against the temperatures, and in the second the logarithms of the vapor pressures are plotted against the reciprocals of the *absolute* temperatures. The best smooth line is drawn through these points by eye, arranging to have the sum total of the deviations on one side of the line equal to those on the other, but giving less weight to points that are far removed from the line. If the data are accurate, the points for the two different series should fall on a single line in each graph. The accepted vapor pressures taken from tables are plotted for comparison.

The second graph is nearly a straight line, and its equation is to be determined. It has the general form

The constants A and B may be found by using the two-point formula for the straight line, using two points directly on the line and far apart.

The empirical equation plotted in this way is tested by substituting into it one or two of the observed temperatures and solving for the corresponding vapor pressures. The calculated vapor pressures should agree closely with the observed pressures.

The heat of vaporization of the liquid is calculated by means of equation (2) and compared with the accepted value taken from tables. The heat of vaporization per gram is obtained by dividing the molar heat of vaporization L by the molecular weight.

The integration of equation (1) shows that the slope of the line obtained by plotting $\log P$ against $1/T$ is equal to $-L/2.303R$. If the line is nearly straight, L may be calculated most accurately by multiplying the slope of the line by $2.303R$. Since L changes slightly with temperatures, accurate measurements will show that the line is not exactly straight. Under these conditions the heat of vaporization at a given temperature should be calculated from the slope of the tangent drawn at the specified temperature. Then equation (2) is not strictly valid.

By using equation (2) and one of the vapor pressures P_1, which falls on the line, the vapor pressure P_2 at some other temperature T_2 is calculated. The temperature coefficient of vapor pressure dP/dT is calculated at one pressure. The reciprocal of this coefficient, dT/dP, is useful for correcting boiling points.

Practical Applications.—Vapor-pressure measurements are important in all distillation problems and in the calculation of certain other physical properties. They are used in the correction of boiling points and in the recovery of solvents. The concentration of vapors in the gas phase may be regulated nicely by controlling the temperature of the liquid. Humidity conditions, which are so important in many manufacturing processes, depend largely on the vapor pressure of water.

Suggestions for Further Work.—The vapor pressure of other liquids may be determined, using, if possible, liquids whose vapor pressures have not yet been recorded in tables. The sublimation temperature of solids may be obtained by covering the thermometer bulb with a thin layer of the solid. The equation for the straight line for the $\log P$ against $1/T$ graph may be determined not by visual graphing but by the method of least squares. It is instructive to check this visual evaluation of the straight-line constants with the least-square evaluation.

The vapor pressure of the liquid may be determined with the isoteniscope,[4] described on page 319, in which the boiling liquid is kept in a small bulb in a thermostat and the removal of dissolved air is shown by a differential manometer.

The vapor pressure may be determined by an entirely different method, evaluating the amount of liquid evaporated by a measured volume of air, as described on page 320.

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6. Surface Tension

A. Capillary-rise Method

Two different methods are given for determining surface tensions of liquids. The relation between chemical constitution and physical properties is illustrated with the parachor, which is calculated from the surface tension and the density.

Theory.—Surface tension is a force pulling inward at the surface of a liquid, tending to make the surface area as small as possible. It is due to the unbalancing of the forces of attraction among molecules, the surface molecules having no molecules to pull them outward.

When a capillary tube is wet by a liquid, the liquid rises in the capillary because this change is in the direction of a decreased surface area. When the liquid reaches equilibrium, the force of gravity pulling downward must be equal and opposite to the force of capillarity pulling upward, and the surface tension γ may be calculated from the rise in the capillary tube h by the following equation:

$$\gamma = \frac{hdgr}{2 \cos \theta} \tag{1}$$

where d = the density of the liquid.
g = the acceleration due to gravity.
r = the radius of the tube.
θ = the angle of contact between the liquid and the walls of the tube.

For most liquids, this angle is so small that $\cos \theta$ is practically 1, and the equation becomes

$$\gamma = \tfrac{1}{2}hdgr \tag{2}$$

When h, r, and g are expressed in c.g.s. units, γ is calculated in dynes per centimeter. The surface tensions are used in calculating parachors defined by the formula of Sugden[3]

$$M \sqrt[4]{\gamma} \tag{3}$$

in which M is the molecular weight and d is the density of the liquid. For more exact work, d may be replaced by the expression $(d-s)$ in

which s is the density of the saturated vapor. By taking differences in the parachors in homologous series it is possible to assign definite atomic parachors to the different atoms. For example, the atomic parachor for carbon is 4.8, hydrogen is 17.1, oxygen is 20.0, chlorine is 54.3, and nitrogen is 12.5. The molecular parachors depend partly on the number and kinds of atoms but partly also on structural features. For example, the presence of a double bond adds 23.2 to the molecular parachor, a triple bond adds 46.6, and a six-membered ring adds 6.1. It is possible then to determine the presence of structural groups in an organic compound from the difference between the experimentally determined molecular parachor and the sum of the atomic parachors.

The critical temperature at which the properties of liquid and gas merge would offer an ideal but experimentally impractical condition for studying relations between physical properties and chemical constitution. At this temperature the surface tension approaches zero. There is some support for the view that under the conditions specified in equation (3) the liquids are being compared under conditions of equivalent molecular energies. At any rate, the concept of the parachor has been very useful in deciding among various structural formulas because it is possible to calculate molecular parachors within 1 per cent from the atomic parachors and the allowances for structural features.

Apparatus.—Capillary tube of about 25 cm length and of 0.2-mm bore; millimeter scale, which is resistant to organic liquids; test tube at least 2 cm in diameter; thermostat at 25°, with glass windows, or large beaker; hand lens (or a cathetometer); benzene, carbon tetrachloride, acetone, or other purified liquids.

Procedure.—The capillary tube is carefully cleaned with *hot* sulfuric acid and potassium dichromate, rinsed with distilled water, and with the liquid to be used if it is miscible with water. In case the liquid to be used does not mix with water, the capillary is dried by drawing *clean* air through it. A tube packed with cotton may be used as a filter. Any dirt or grease in the capillary will introduce an error. Compressed air from a pump cannot be used on account of the oil droplets that it carries.

The tube is wired to the millimeter scale, and supported by a stopper which fits into the mouth of a wide test tube, as shown in Fig. 6. The apparatus is placed in a thermostat at 25°, provided with windows so that the scale may be read while the apparatus is immersed. It is now generally accepted that 25°C. is the standard temperature for physical-chemical measurements. A large beaker of water stirred and regulated by hand to 0.1° may be used in place of a thermostat. The

purified liquid is poured into the test tube, to a depth sufficient to provide a flat meniscus. The stopper is replaced, a clean dust-free rubber tube is fitted with a loose wad of cotton to keep out dirt and spray and attached to the projecting tube as shown. After coming to the temperature of the thermostat the liquid in the capillary is raised slightly by gently blowing into the rubber tube, and allowed to fall back to its equilibrium level. Then it is depressed by slight suction. If the capillary is clean, the reading on the scale should be the same after raising the level as after depressing it.

Fig. 6.—Surface tension by capillary rise.

The difference in the level of the liquid in the capillary tube and in the test tube is read on the scale, the bottom of the meniscus being read in each case. The wide test tube gives practically a flat meniscus. A reading lens may be used if special care is taken to avoid parallax, but greater accuracy is attained with a cathetometer (page 415).

Four or five measurements are made on each liquid, and averaged. The top of the column of liquid should be kept at approximately the same position in the capillary for the different liquids. This may be accomplished by immersing the bottom of the capillary to the proper depth.

The radius of the tube is obtained in two different ways. The capillary rise is observed with pure water, the surface tension of which is known to be 71.8 dynes per centimeter at 25°C. At least five observations are made. The averaged value of h is obtained from the scale readings, and r is obtained by solving equation (2), using the known value of γ. As a check on the value of r, the capillary tube is partly filled with mercury, the length of the column is carefully measured, and the mercury is poured out and weighed. The radius is calculated on the assumption that the bore of the tube is circular. The two methods should check closely, but the surface-tension method probably gives the better results.

Measurements of the capillary rise are made on at least three purified liquids, on an unknown liquid supplied by the instructor, and on water.

Calculations.—The several readings of the capillary rise are averaged for each liquid, and the surface tension is calculated with the

help of equation (2). The densities at 25° are as follows: water, 0.997; benzene, 0.875; carbon tetrachloride, 1.584; and acetone, 0.790. The densities of other liquids may be determined experimentally or obtained from tables.

The average error in the readings is calculated. The calculated values of surface tension are compared with accepted values given in tables, and the percentage error is calculated. One of the most common causes of failure to check with accepted values lies in the existence of impurities contained in the liquid under examination, and of course this difficulty is not removed by taking more readings or by improving techniques.

The parachors for each liquid are calculated by equation (3) and compared with the sum of the atomic parachors. The structural features are identified, such, for example, as the presence of a double bond or a six-membered ring.

Practical Applications.—Surface tension is an important phenomenon in the study of emulsions and colloid chemistry. It is an important factor in the concentration of ores by the flotation process. Surface-tension measurements find valuable applications in the biological sciences, particularly in bacteriology; the movement of the moisture of the soil and the passage of sap in plants are only two of the many agricultural phenomena that involve surface tension.

Suggestions for Further Work.—The surface tensions of several different liquids may be measured.

The parachors may be calculated and used to check the existence of structural features such as double bonds.

The surface tensions may be determined in an ice and water bath, and again at 35 to 50° in a large beaker of stirred water the temperature of which is regulated by hand. The connection with the critical temperature t_c is given by the Ramsay-Shields-Eötvös[5] equation

$$\gamma = 2.12(t_c - 6° - t)$$

In certain polar liquids such as water and the alcohols, the value of the molecular weight M becomes abnormally large if the empirical constant 2.12 is retained. In such cases it is probable that the molecules are drawn more tightly together into larger aggregates.

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B. Torsion-balance Method

Theory.—The theory is discussed under Exp. 6*A*.

In the torsion-balance method, the surface tension is determined in a simple way, by measuring the force necessary to pull a ring of platinum wire from the surface of the liquid. The force is measured by the torsion on a wire, attached to a circular scale, the readings of which can be calibrated directly in terms of surface tension. Special balances are also made for such measurements.

Apparatus.—DuNouy surface-tension apparatus;[1] watch glass; purified liquids; 1° thermometer; solutions.

Procedure.—The DuNouy apparatus is shown in Fig. 7. The ring of platinum wire is cleaned with *hot* cleaning solution of sulfuric acid
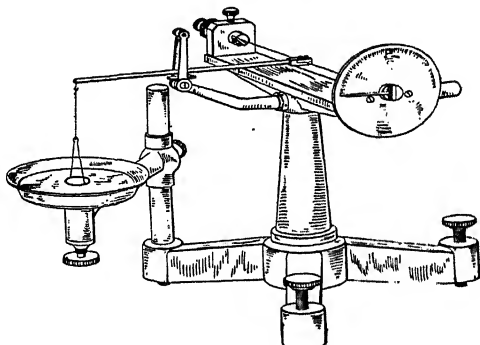
Fig. 7.—DuNouy apparatus for measuring surface tension.

and potassium dichromate, thoroughly rinsed with warm distilled water, and dried by carefully touching with a clean filter paper or cloth and allowing to stand in the air. Occasionally, the ring may be heated momentarily in a Bunsen burner if further cleaning is necessary. It must not be touched with the fingers, and care should be used not to bend it. The apparatus is adjusted by hanging the ring in the hook, and turning the knob at the right until the pointer is at zero. The set screw at the back is then turned until the lever nearly touches the arm at the left. It must not actually touch, but the gap must be very small. The platform holding the watch glass with the liquid is now raised until the liquid just touches the ring. The knob at the right is then turned slowly and steadily until the ring is suddenly torn from the

surface of the liquid. The guard above the lever is adjusted so that the ring cannot be thrown off the edge of the watch glass.

As the pointer is turned, the ring pulls away slightly from the watch glass before it breaks the film and the beam is raised above its original horizontal position. To compensate for this error, the platform is lowered gradually while the pointer is turned, so that the beam is at its horizontal position when the ring is pulled off. If this adjustment is not made, the readings will be too high.

Several readings are taken on each liquid; these should agree closely.

One of the errors in this method lies in the lack of temperature control, for the evaporating liquid is irregularly cooler than the room. The surface temperature is estimated by partly immersing a thermometer in the liquid and wetting the bulb.

There are other errors involved[4] as, for example, the weight of the ring pulled off from the surface is increased by drops of adhering liquid. Moreover, the cylindrical film of liquid is spread out at the moment of breaking so that its diameter does not coincide with the diameter of the ring. Corrections for these factors can be made, but they are not necessary in some types of work, especially where changes of surface tension rather than absolute values are important.

After the determinations have been made, the instrument is calibrated over the range of scale readings involved. The ring is dried, a weighed square of paper is inserted, and a fractional gram weight is added. The pointer is turned until the lever just barely clears its support and lies in its standard horizontal position. The weight of paper and fractional gram weight divided by the scale reading and multiplied by 981 gives the value in dynes of one scale division. The calculation is repeated once or twice, using more weights.

The surface tensions of water and three or four organic liquids are determined, but the absolute values will not agree very well with those obtained by the capillary-rise method.

A dilute solution of sodium stearate in water (about 0.01 g in 100 ml of water) is freshly prepared, and the surface tension is determined at intervals of a few minutes for nearly half an hour.

A change of surface tension with time indicates a changing concentration in the surface layer. The influence of concentration on surface tension is studied with mixtures of approximately $0.1M$, $0.01M$, and $0.001M$ acetone or alcohol in water.

The influence of other cleansing materials such as soaps or Dreft on the surface tension of water may be determined.

The influence of salts such as sodium chloride and magnesium sulfate on the surface tension of water may be

Calculations.—If the torsion of the wire is directly proportional to the angle through which the pointer is turned, the various calibration values will be approximately the same, and an average value may be taken. The scale reading for each liquid is multiplied by this proportionality factor. If the proportionality factor changes in different parts of the scale, it is necessary to plot weights against the scale readings and take an interpolated value. Since there are two surface films pulling down, one outside and one inside the ring, the surface tension in dynes per centimeter is obtained by dividing the force in dynes registered on the scale by twice the circumference of the ring. Usually the circumference is exactly 4 cm.

Practical Applications.—These are discussed under Exp. 6A.

Suggestions for Further Work.—Measurements are made so rapidly with the DuNouy apparatus that the surface tension of a large number of liquids, solutions, and colloidal solutions may be determined. If a solute lowers the surface tension it concentrates in the outer layers of the solution, but if it increases the surface tension of the solution it is driven away from the surface. Surface tension then is never increased very much by the addition of a solute, but it may be decreased by a considerable amount. This theory may be checked by a number of determinations. An improved instrument is now available, operating as a "chainomatic" balance.

A simple instrument that can be constructed in the laboratory has been described by Lloyd and Scarth.[2]

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Additional references are given under Exp. 6A.

7. Surface Tension

A. Drop-weight Method

Theory.—When a liquid is allowed to flow slowly and vertically through a capillary tube with ground tip, a drop of the liquid will form on the tip and will increase in size. The weight of the drop, as it is about to fall by detaching itself from the tip, is balanced by the upward pull of the surface tension around the periphery of the drop. The weight of the drop that falls should be

$$mg = 2\pi r\gamma$$

in which m is the actual mass of the drop, r is the outer radius of t tube, and γ is the surface tension in dynes per centimeter, and g the acceleration of gravity.

Actually only a portion of a drop (or of several drops) falls, and Harkins and Brown propose the formula

$$m_i g = 2\pi r \gamma \qquad (2)$$

where m_i, the mass of an "ideal" drop, is equal to $m/f(r/V^{1/3})$. Here $f(r/V^{1/3})$ is the fraction of the ideal drop falling, and, r is the outer radius of the tube; and V, the actual volume of the drop falling, is
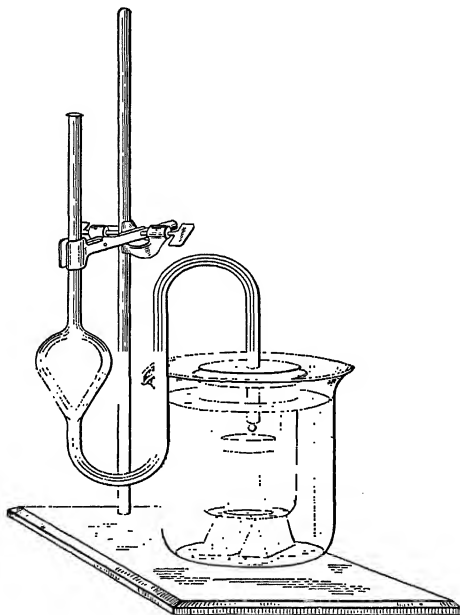
Fig. 8.—Surface tension by drop weight.

calculated from the weight and density of the drop. Best results are obtained when tips are chosen such that $r/V^{1/3}$ is between 0.7 and 1.0.

Apparatus.—Drop-weight surface-tension apparatus with ground tip; purified liquids; thermometer.

Procedure.—A useful form of apparatus for the measurement of surface tension by drop weight is shown in Fig. 8. Before the performance of the experiment the bulb and capillary should be scrupulously cleaned. Hot chromic-sulfuric acid and distilled water are effective agents. After the apparatus has been conditioned and assembled, a

dried weighing bottle is placed under the tip and the cover is moved into position. The liquid whose surface tension is to be measured is filled into the bulb and capillary, and the liquid levels are adjusted until the time rate of formation of a drop is of the order of 5 min. The difference in liquid level to meet this requirement is ordinarily less than 1 cm.

The first drop is allowed to form over the relatively long period of time in order to saturate the space within the container. After the detachment of this first drop, additional pressure is carefully applied in the formation of the remaining drops, but care must be taken that each drop falls only under the force of gravity. After the first drop, 30 sec. suffice for the formation of the others. A total of 20 to 25 drops should be adequate for the determination. The weighing bottle may be cooled in ice water before it is removed from the apparatus to prevent loss by evaporation during the weighing process.

Water, benzene, and carbon tetrachloride are suitable liquids for the determination.

Calculations.—The surface tensions of the several liquids are calculated from the drop weights by means of equation (2). If the capillary tip is chosen and ground so that the value of $(r/V^{1/3})$ lies between 0.7 and 1.0, $f(r/V^{1/3})$ may be taken as 0.60. For other values of $(r/V^{1/3})$ the correction tables of Harkins and Brown[2] are to be consulted.

The average error in the readings is computed, and comparisons between calculated and tabular values of surface tension are made. The parachors for each liquid may be calculated by equation (3) of the previous experiment.

Practical Applications.—These are discussed under Exp. 6.

Suggestions for Further Work.—It is of interest to study the capillary activity of a series of fatty acids in aqueous solution. For the observations, formic acid, acetic acid, propionic acid, and butyric acid solutions in water at concentrations $0.1N$, $0.25N$, and $0.5N$ are used. The temperature should be maintained constant at a convenient figure in all cases. If the results are plotted with surface tension as a function of concentration, the rule of Traube may be demonstrated.

References

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2. HARKINS and BROWN, *J. Am. Chem. Soc.*, **41**, 519 (1919); I.C.T. IV **435** (1928).
3. FREUNDLICH, "Colloid and Capillary Chemistry," pp. 21*ff.*, E. P. Dutton & Company, Inc., New York (1922).

B. BUBBLE-PRESSURE METHOD

Theory.—By reversing the position of liquid and gas in the drop-weight experiment one obtains what is described as the bubble-pressure

method for the determination of surface tension. The theory corresponds fairly closely with that for the drop-weight method. In the case of a bubble of gas under the surface of a liquid the force holding the two hemispheres together is $2\pi r\gamma$. This force is also equal to the pressure times the cross-sectional area, or $\rho\pi r^2$. Since the two forces are equal

$$\rho = \frac{2\gamma}{r}$$

If air (or other gas) is forced through a capillary tube immersed in a liquid until the surface of the liquid is just forced down to the plane of the outlet, the pressure is hdg, where h is the height of the column of liquid and d is the density. As the pressure is increased, a bubble forms which eventually breaks away. At any time the total pressure applied is equal to the pressure of the immersion (hdg) plus that pressure which is required to form the curved surface ($2\gamma/r$), or

$$P = hdg + \frac{2\gamma}{r} \tag{1}$$

Since for any given depth of immersion of the tube hdg is constant and γ is also constant, the total pressure will rise to a maximum value to give r its minimum value, *i.e.*, when it is equal to the radius of the capillary.

In the experiment the capillary tube is maintained at a given depth of immersion and the maximum pressure P which just causes the bubble to detach itself is measured. Then

$$\gamma = \frac{r}{2} \left(P_{\text{max.}} - hdg\right) \tag{2}$$

Apparatus.—Clean capillary tube with radius of bore about 0.3 mm, water manometer; beaker; water, benzene, and glycerol.

Procedure.—Capillary tube and water manometer are assembled as shown in Fig. 9. The tube may be prepared by drawing a larger tube down so that its bore radius is about 0.3 mm. A sharp fracture at the end of the tube is obtained by scratching the thin wall of the tube with a file and breaking the tube at this scratch point. The capillary is mounted vertically and connected by rubber tubing to the manometer.

The beaker is nearly filled with the liquid whose surface tension is to be determined, and the tip of the capillary tube is immersed to a known depth below the surface of the liquid. Two or three centimeters depth of immersion is suggested. By a simple manipulation the water level in one of the leveling tubes may be maintained at some convenient

reading. The levels are slowly raised to give the difference in height (hydrostatic pressure) which is required to detach an air or gas bubble from the end of the capillary tube. Four or five measurements are made for each liquid, and the average is used in the computations. The experiments are performed at 25°C.

The radius of the capillary tube at the point of formation of the bubble is obtained in two ways. The maximum bubble pressure is
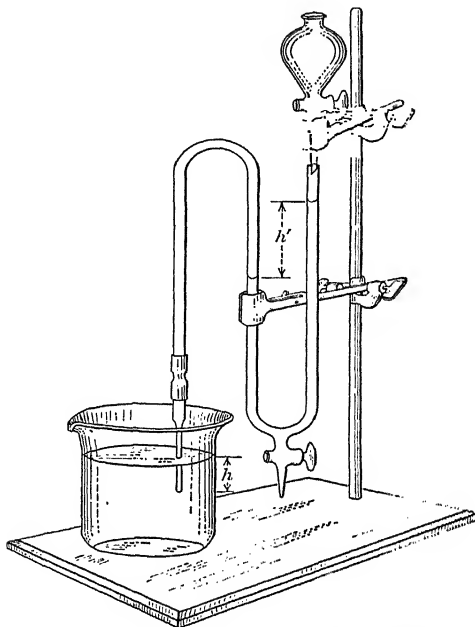
FIG. 9.—Surface tension by bubble pressure.

observed with pure water, the surface tension of which is known to be 71.8 dynes per centimeter at 25°C. The averaged value of the maximum bubble pressure and depths of immersion of capillary are used with equation (2) to calculate the effective radius of the tube. For a check determination the inside diameter of the capillary at the tip is measured directly by using a micrometer microscope, or a filar micrometer. Six readings at angles of about 60 deg. should be taken and averaged.

Measurements of maximum bubble pressure are made with other purified liquids such as benzene and glycerol.

Calculations.—The several readings of the pressure just required to displace an air or gas bubble from the end of the capillary tip are averaged for each liquid, and the surface tension is calculated with the help of equation (2). The densities of the several liquids are available in standard tables. The acceleration due to the earth's gravitational field is 981 cm per second per second.

As usual, readings are averaged and comparisons with accepted surface tension values are made.

Practical Applications.—The method of maximum bubble pressure is useful for the determination of surface tension of more viscous liquids. It has been used successfully for this purpose with lighter road oils at room temperatures and with heavier road oils at somewhat elevated temperatures. As an example of a more viscous liquid, glycerol has been suggested as one of the liquids for this experiment.

Suggestions for Further Work.—The suggestions made in connection with Part A of this experiment may be consulted.

References

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8. Viscometry

Experience is given in the determination of viscosities of pure liquids and mixtures by using a capillary-tube method. Densities are measured with a Westphal balance.

Theory.—Resistance is offered when one part of a liquid is moved past another. This internal friction or resistance to flow is determined by the viscosity of the liquid.

The viscosity of a liquid is usually measured by observing the rate of flow of the liquid through some form of capillary tube. For accurate viscosity determinations, a steady flow parallel to the axis of the tube must be maintained, and its rate must not exceed a certain value, which is dependent on the viscosity of the liquid and the radius of the tube.

The law that expresses the viscous flow of liquids through such tubes was first deduced by Poiseuille. This law gives the relation between the coefficient of viscosity η, the volume v of liquid flowing across the whole cross section of the tube in unit time, the pressure p, and the radius r and length l of the tube. It is expressed as follows:

$$\eta = \frac{\pi p r^4}{8vl}$$

This is the fundamental equation of viscometry.

The experimental determination of the absolute viscosity of a liquid is a difficult task, but the measurement of relative viscosity, the ratio of the viscosity of a liquid to that of some standard liquid such as water, is simple and adequate for most purposes. The absolute viscosity may be calculated if necessary from a knowledge of the absolute viscosity of the reference liquid. In a simple viscometer, the pressure driving liquid through the capillary depends on the height h, through which the liquid falls, its density d_1, and the acceleration due to gravity g, and is given by the expression $h \times g \times d_1$. If *exactly* the same volume of a second liquid is introduced into the tube, the pressure driving liquid through the tube depends on the magnitude of the product $h \times g \times d_2$, where d_2 is the density of the second liquid. The driving force, therefore, is proportional to the densities of the two liquids. If the same volume of the two liquids is used, the times of efflux for this volume are proportional to the driving force. This statement is expressed mathematically by the equation

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2}$$

where η_1 and η_2, d_1 and d_2, t_1 and t_2 are the viscosities, densities, and times of efflux, respectively, for the two liquids.

Apparatus.—Viscometer; stop watch; thermostat with glass window; 5-ml pipette; Westphal balance or other means for determining densities; acetone; benzene, carbon tetrachloride, or other organic liquids.

Procedure.—The viscometer shown in Fig. 10 is the Ostwald modification of Poiseuille's apparatus. After the viscometer has been thoroughly cleaned with hot sulfuric acid and potassium dichromate, it is rinsed and dried by aspirating through clean air from the laboratory. Traces of oil from compressed air or other dirt may cause serious errors. The viscometer is clamped vertically in the thermostat in such a position that it can be viewed easily, and exactly 5 ml or other specified quantity of water is added from a pipette. A dust-free rubber
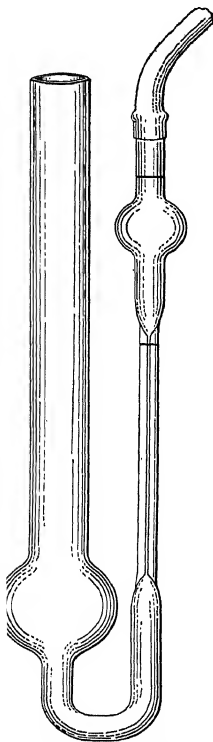
Fig. 10.—Ostwald viscometer.

tube loosely plugged with cotton is attached to the smaller tube, and the liquid is drawn up into the enlarged bulb and above the upper mark. The quantity of liquid must be sufficient to fill the lower bend and extend up slightly into the larger tube.

The liquid is then allowed to flow down through the capillary, and the stop watch is started when the meniscus passes the upper mark and stopped when it passes the lower mark. Four or five check determinations on the time of outflow are made. If they do not agree closely, the tube should be cleaned again.

The measurements are repeated on two or three pure organic liquids such as acetone, carbon tetrachloride, benzene, and methanol, drying each time before the new liquid is pipetted into the viscometer.

A determination is made on an "unknown" liquid or mixture of liquids.

The relative viscosities of solutions of acetone and water are measured by making up solutions of 0.25, 0.50, and 0.75 mole fraction. Solutions of methanol and water or other pairs of organic liquids may be used instead of the acetone and water.

For the calculation of viscosities it is necessary to know the densities of the pure liquids and the solutions. A Westphal balance, or better, a chainomatic density balance may be used (page 321).

Calculations.—The relative viscosities are calculated by taking the viscosity of water as unity and using the formula given above. The relative viscosities are then changed to absolute viscosities in poises by multiplying by the absolute viscosity of water, which at 25° is 0.00895. When possible, the absolute viscosities are compared with accepted values given in tables.

The measurements on solutions are best represented by means of a curve in which the mole fraction (page 453) of one of the components, which may be designated as the solvent, is plotted along the x-axis, and the viscosity relative to that of the pure, unmixed solvent is plotted along the y-axis. The shape of the curve obtained in this manner gives information concerning the changes that take place upon solution.

Practical Applications.—Viscosity measurements are important in lubrication and in the movement of liquids through pipes. They find application also in physiological studies.

Suggestions for Further Work.—Other pairs of liquids may be chosen from among the following list, some of which form ideal solutions, some indicate some type of chemical interaction, and others show a breaking down of larger units into smaller molecules in the presence of the second liquid: acetone-chloroform; benzene-nitrobenzene; carbon tetrachloride-ethanol; chloroform-ethanol; ethanol-methanol; benzene-carbon tetrachloride.

The viscosity of liquids may be determined at several different temperatures to test the empirical relation that the logarithm of the viscosity is directly proportional to the reciprocal of the absolute temperature for nonassociated liquids. The viscosity of nitrobenzene may be determined, for example, at 25°, at 50°, using a hot water bath, and at the temperature of boiling water. The density of nitrobenzene is 1.17 at 50° and 1.123 at 100°. Log η is then plotted against $1/T$.

Another interesting study lies in testing the suggestion that the larger the molecule, the greater the viscosity.

If the reciprocal of viscosity (the fluidity) of a solution is plotted against mole fraction, a straight line is obtained when the solution is ideal, *i.e.*, when the components have no apparent chemical effect on each other and the properties of the two components are additive. It is interesting to apply this test to these or other solutions.

Viscosities may be determined by the method of the falling sphere (page 326). A 2-mm ball bearing is allowed to drop through 25 cm in a 20-cm tube, and the times of falling are observed. The results are compared with those obtained with the capillary tube.

In the hands of Staudinger and his associates, viscosity measurements on solutions of highly polymerized linear molecules have acquired considerable significance. A theory has been developed making it possible to estimate the molecular weights of the solutes from the changes in viscosity produced by them, provided that the solutions are sufficiently dilute. Such work requires the use of very accurate timing devices.

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8. SHEPPARD and HOUCK, *J. Rheology*, **1,** 349 (1930).

CHAPTER III

OPTICOCHEMICAL MEASUREMENTS

9. Spectrometry

The calibration and use of the spectrometer is illustrated in this experiment for both emission and absorption spectra. Unknown mixtures are analyzed, spectra of colored substances mapped, and the simplest type of spectral series calculated.

Theory.—The separation of light into its various wave lengths by refraction through a prism constitutes one of the most important operations in physical chemistry. White light is spread out into a complete spectrum, the light of short wave lengths being refracted more than that of the longer wave lengths. The visible range of the spectrum extends from the violet at 4,000 Å (4,000 × 10⁻⁸ cm) to the red at 8,000 Å (8,000 × 10⁻⁸ cm), and for this region prisms and lenses of glass are adequate. For the still shorter wave lengths of the ultraviolet, quartz or fluorite is used; and for the longer wave lengths in the infrared, rock salt or fluorite is used.

Light emitted by incandescent vapor is spread out by a spectrometer into bright lines of different colors, each line being an image of the slit through which the light enters the instrument. These lines are used in the identification of materials, for each substance has its own characteristic wave length or wave lengths. The wave lengths of these lines give important information regarding the structure of the atoms and molecules and the electron displacements taking place within them.

When white light is passed through an absorbing medium, light of certain wave lengths is absorbed by the molecules, through the agency of electron displacements, and converted eventually into heat or, less frequently, into chemical action. These wave lengths, then, are missing, and corresponding dark regions appear in the otherwise continuous spectrum. The dark Fraunhofer lines in the sun's spectrum are due to absorption by the gases surrounding the sun or the earth.

Apparatus.—Spectroscope; nichrome (or platinum) wires; frosted electric light; dark room or darkened box; chlorides of sodium, potassium, lithium, calcium; capillary mercury arc; glass absorption cell; potassium permanganate; methyl orange or dyes; gas discharge tube, containing hydrogen; induction coil; color filters.

Procedure.—A sketch of the spectroscope is shown in Fig. 11. The collimator renders the rays of light parallel; the prism refracts them to an extent depending on their wave length; and the telescope focuses them on the exit slit, where they are examined through the magnifying lens of the eyepiece. Light from a small lamp passes through a transparent scale on a black field and strikes the rear face of the prism at an oblique angle such that the image of the scale is reflected to the exit slit and eyepiece.

The spectroscope is set up in a darkened room with a small electric light for illuminating the scale and slit. When properly adjusted, the
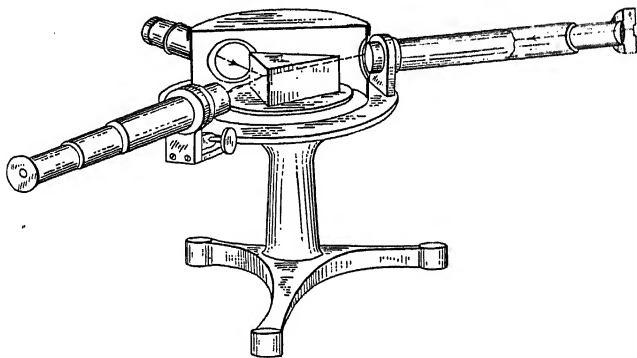
FIG. 11.—Spectrometer.

slit image for sodium appears narrow and sharp on a scale which is clear but not too bright.

The scale is calibrated first with the well-known lines of the mercury spectrum. Convenient and inexpensive capillary mercury lamps (100 watts) are now available (page 392). The lamp must be placed in a box for protection of the eyes, a small slit being cut for the illumination. The position of each prominent line on the scale is recorded, using a narrow slit. A few other spectral lines are recorded for calibration of the scale, by using the incandescent alkali or alkaline earth salts. The salts are volatilized in a colorless Bunsen flame on a nichrome wire about 0.5 mm in diameter set into a holder and supported in a clamp. Platinum wire sealed into glass is better but more expensive. The burner must be at least 15 cm in front of the slit to avoid injury to the optical parts. The wire is thoroughly cleaned by rubbing off any particles of salt adhering to it, dipping it into a small beaker of hydrochloric acid, and heating it in the flame. The process is repeated, and

the wire is dipped into uncontaminated acid and heated. When the wire is so clean that practically no color is produced, it is plunged while red hot into the salt on a watch glass. When the wire becomes badly contaminated, it is replaced with a new one. The wire is supported in the flame but must be below the level of the slit, because it gives off a continuous spectrum.

The chlorides of sodium, potassium, lithium, and calcium are convenient for calibrating the scale. Difficulty may be experienced in locating the violet lines of potassium and calcium, for they are faint and disappear soon after the salt is placed in the flame. The difficulty may be overcome by having plenty of salt on the wire, widening the slit, reducing the scale illumination, and taking a reading as soon as the salt is introduced. For the final readings, the slit should be as narrow as possible.

After calibrating the scale, unknown salts or mixtures of salts are to be analyzed qualitatively, the elements present being identified by measuring their wave lengths and referring them to any standard table of wave lengths. Only the most prominent lines in these tables need be considered. If the readings are not all made on the same day, the setting of the scale should be checked by the position of the sodium line. If the unknowns are not easily volatile, they should be moistened with concentrated hydrochloric acid.

The spectrum of hydrogen at low pressure in a Geissler tube is accurately measured, the scale readings of each prominent line being recorded. The gas is excited with a small induction coil such as an automobile coil or by a small Tesla coil operating on the 110-volt a.-c. circuit.

Absorption Spectra.—The absorption spectrum of a colored salt such as potassium permanganate or a dye solution may be obtained in the following manner. The absorption cell is filled with a 1 per cent solution of potassium permanganate and placed in the holder in front of the slit. A small, frosted electric light bulb is used as the source of illumination. The outside limits of the dark bands are recorded. A solution half as concentrated is prepared by diluting 10 ml of the solution with 10 ml of distilled water, and the spectrum is again examined. Solutions one-fourth, one-eighth, one-sixteenth, etc., as concentrated are made by successive dilutions, and their absorption spectra are recorded. The dilution is continued until the absorption has disappeared. The appearance and location of the absorption band just before the final dilution are recorded. Most colored liquids and solids give absorption bands that are much broader and less sharply defined than the emission lines of incandescent gases. Potassium permanga-

nate and especially salts of neodymium and praseodymium give fairly sharp bands in sufficiently dilute solutions.

A great many salts and organic compounds, however, have absorption bands which, though not sharp, serve as a means of identification. Several common colored substances are examined qualitatively, recording the regions of maximum absorption, *i.e.*, the wave lengths at which absorption still persists in dilute solutions. Among these may be included some of the following aqueous solutions: copper sulfate, copper sulfate with excess of ammonium hydroxide, potassium dichromate, methyl orange in acid and in alkaline solution. Corning glass filters or photographic filters and didymium glass are recommended.

The influence of hydration on the color of an ion may be illustrated by examining in the spectroscope a dilute solution of pink cobalt chloride, to which is added a considerable quantity of anhydrous calcium chloride in one case and alcohol in another.

Calculations.—The scale is calibrated by drawing a graph constructed with scale readings as abscissas and with wave lengths given in the following list, as ordinates. A smooth curve extending from the red lithium or potassium line to the violet mercury or potassium line is drawn through the points plotted. The wave length corresponding to any scale division is found by interpolation.

WAVE LENGTHS OF SPECTRAL EMISSION LINES

Metal	Å	Metal	Å
Li	6,710	Ca	5,530
K	7,680	Hg	5,461
Ca	6,260 6,180	Hg	4,359
		Ca	4,230
Na	5,896 5,890	Hg	4,047
		K	4,040
Hg	5,791 5,769		

Some of these lines are really groups of lines, and some near-by lines are not included. The yellow doublet of sodium appears to be a single line unless the resolution of the spectroscope is quite good. It is so intense that it shows up as an impurity in almost every salt. The many orange lines of calcium are grouped together in a broad band.

Absorption spectra may be mapped by drawing rectangles with wave lengths plotted horizontally for each successive dilution, and by shading the regions corresponding to the absorption bands at each dilution. More scientifically, the results may be represented on a

graph in which the logarithms of the concentration are plotted against wave lengths of the edges of the absorption bands.

The mathematical analysis of the spectrum of hydrogen by Balmer laid the foundation for the remarkable advances that have been made in correlating and explaining the various spectra. Expressing the lines of the hydrogen spectrum in wave numbers, they can all be fitted into a general formula of the type $R\left(\dfrac{1}{2^2} - \dfrac{1}{n^2}\right)$, where n has the value 2, 3, 4, 5, 6, etc., for successive lines, and R is the Rydberg constant 109,677.76.

The hydrogen spectrum contains several lines, but there are three prominent ones due to atomic hydrogen which should be picked out and measured accurately. They fall in the general regions around 4,000, 5,000, and 6,500 Å. The observed wave lengths are converted into wave numbers and compared with the calculated wave numbers. The wave number, or the waves per centimeter, is the reciprocal of the wave length in vacuo expressed in centimeters. For example, the wave number of the sodium line is $\dfrac{1}{5,890 \times 10^{-8}}$, or 16,900.

Practical Applications.—The spectroscope has been one of the most useful tools in the advancement of science, particularly in the fields of chemistry, physics, and astronomy. With it, most of the elements and many compounds may be identified, even in minute quantities. It has aided in establishing the structure of organic compounds. It has been responsible for the discovery of many of our elements. It has made possible a determination of the composition and temperature of the sun and stars. Even the velocities of some of the stars have been calculated with its help. Intelligent advances in photochemistry demand a complete knowledge of absorption spectra, and a spectrometer furnishes the best source of monochromatic illumination for controlled experiments in that branch of physical chemistry.

Suggestions for Further Work.—Complex spectra such as those of barium and strontium may be determined and compared with the spectra recorded in tables.

Absorption spectra of blood, green leaves, and various common materials may be mapped.

Photographs of spectra may be made either with standard equipment or by substituting for the telescope tube another tube of proper length carrying a camera having a ground glass for fôcusing.

The helium spectrum may be determined and fitted with a formula similar to that used for hydrogen.

References

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2. BAKER, "Spectrum Analysis," Baillière, Tyndall & Cox, London (1923).
   Additional references are given on pages 67 and 298. Many articles on practical uses of spectrometry are to be found in the current literature.

10. Refractometry

Experience is obtained in the operation of different kinds of refractometers. They are used to analyze mixtures, to test for purity, and to decide questions of molecular structure.

Theory.—Whenever light passes into a transparent medium, a small part of the ray is reflected back while the other part is propagated in the second medium and is known as the "refracted ray." This refracted ray does not continue in the same direction as the incident ray, but is bent at the point where it enters the second medium. The angle that this ray makes with a normal drawn to the surface of the second medium at the point where the light enters is known as the "angle of refraction." The index of refraction n of any medium with reference to air is defined as the ratio of the velocity of light in air to the velocity of light in that medium. It is defined also by the equation $n = \sin i/\sin r$, where i is the angle of incidence, and r is the angle of refraction. This index of refraction is characteristic of each particular substance, and its measurement is a matter of considerable practical importance.

Apparatus.—Pulfrich refractometer; Abbe refractometer; immersion refractometer; benzene, carbon tetrachloride, acetone, or other purified liquids, nitrobenzene and toluene; sodium or potassium chloride or other purified salt; sodium-vapor lamp or other source of monochromatic light.

Procedure.—The *Pulfrich refractometer* is shown in diagrammatic form in Fig. 12. It depends on the principle of grazing angles, and the deviation of the light that enters at the grazing angle (practically parallel to the face of the prism) is measured. Light rays that strike the prism surface obliquely are refracted downward into the prism. Light rays that are inclined upward from the line parallel to the surface miss the prism entirely or hit the ground-glass lip and are scattered. The line indicated with arrows shows the line of demarcation between the dark and light fields. The angle of deviation for this sharp edge of the light field is measured with an accurate telescope moving across a circular scale graduated in fractions of degrees.

A sodium-vapor arc lamp (page 393) is the best source of light for this refractometer. A crystal of rock salt placed on top of a Méker gas burner is fairly satisfactory. A capillary mercury arc with suitable filters (pages 392 and 395) gives a good light as does also a Geissler tube of hydrogen or helium operated by a small induction coil. The light must be carefully focused for maximum intensity and definition.

The zero setting of the instrument is obtained by holding an electric lamp close to the small square window in the telescope tube near the

eyepiece and turning the graduated circle, which carries the telescope, until the image of the cross hairs, at the left of the field (Fig. 12), coincides with the cross hairs. If the two do not coincide, one reading is taken when the upper hair coincides with its image, a second one is taken when the lower hair coincides with its image, and the two readings are averaged. The window at the right is in reality a right-angled

Field of View   Zero Adjustment
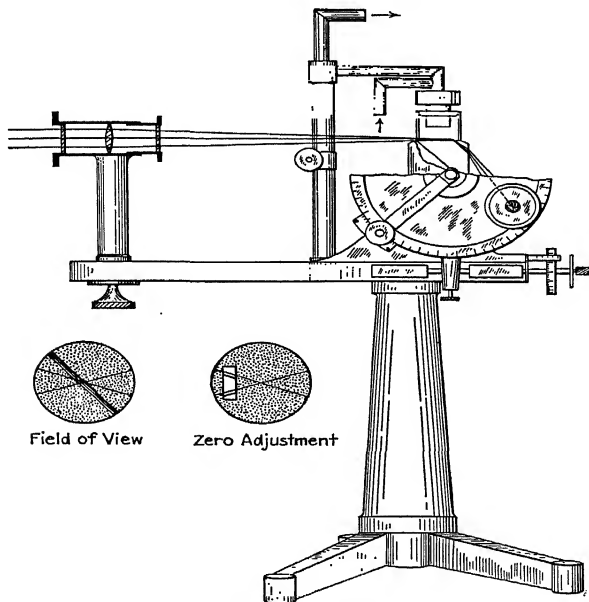
FIG. 12.—Pulfrich refractometer.

prism, which transmits the light down the telescope tube to the face of the main prism where it is reflected back to give the square of light at the left. When the shadow of the cross hairs at the right coincides with the image at the left, the refractometer is in adjustment, and the reading of the scale for this setting must be subtracted from (or added to) any reading for refractive index.

One or two milliliters of various pure organic liquids is used for examination. The liquid is introduced into the cylindrical glass cup with a pipette, care being taken not to scratch the face of the prism. The cements used are given on page 331. They are attacked by water

and acetone. The brass cap is set down into the cup, and the stopcocks are opened so that the liquid is kept at constant temperature by the circulation of water from the thermostat. The circular scale is turned until the intersection of the cross hairs just touches the *upper* edge of the yellow line. If light from the room interferes with the observations, a black cloth or paper is placed over the instrument. The final adjustment is made with the micrometer screw at the bottom of the wheel. Four or five readings of the angle are taken for each liquid and averaged.

When the readings have been completed, the liquid is sucked out and the last traces are taken up carefully with filter paper. If the liquid is nonvolatile, the cup may be rinsed out thoroughly with a volatile solvent. These operations must be carried out cautiously because the cement holding the cylindrical cup to the prism is not strong. As a rule it cannot be used with aqueous solutions on account of its solubility.

The refractive indices of three different pure organic liquids are determined. Benzene, carbon tetrachloride, and other liquids are suitable.

The refractive index n is calculated from the formula

$$n = \sqrt{N^2 - \sin^2 i} \tag{1}$$

where N equals the refractive index of the glass prism against air and $\sin i$ equals the sine of the angle i of emergence, measured on the circular scale.

The value of N is furnished with the instrument. Tables giving the refractive index corresponding to angles for every 10 sec. are also furnished, but a complete calculation should be made according to equation (1), for one of the liquids. The refractive index is usually calculated for the yellow D line of sodium. Other wave lengths may be used, as described on page 332.

The refractive index of each liquid is compared with the accepted value given in tables if they are available for the given temperature. If there is serious discrepancy, the liquids may be impure. Distillation with an efficient column and a large reflux ratio (page 83) is an excellent general method of purification. After calculating the refractive index, the specific refraction r is calculated by the formula of Lorentz and Lorenz

$$r = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$$

and it is multiplied by the molecular weight to give the mo refractivity. The values for the density d of the liquids may be

obtained from the Landolt-Börnstein "Tabellen" or the International Critical Tables, or they may be determined experimentally.

The presence of double bonds in benzene and of ketone oxygen in acetone should be established from the experimental value of molecular refractions and tables of atomic refractions.

The *Abbe refractometer* is shown in Fig. 13. Light from a frosted electric lamp is reflected up into the first prism where, at the farther
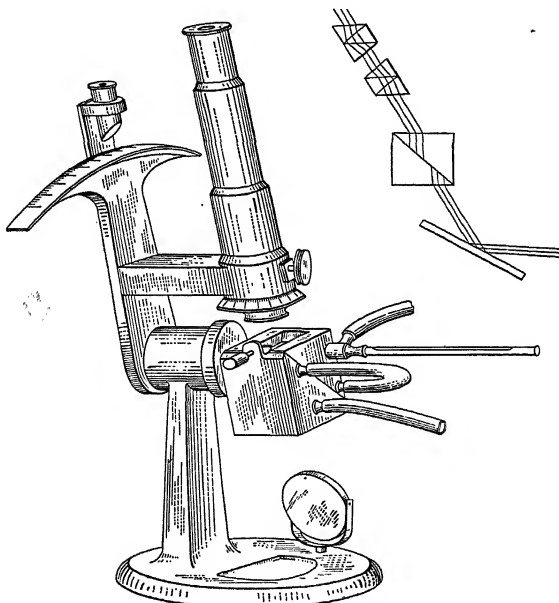
FIG. 13.—Abbe refractometer.

side, it is scattered by the ground-glass surface, and it then enters the thin film of liquid between the two prism surfaces. The light that hits the smooth face of the upper prism at the grazing angle, or at a smaller angle, enters the second prism and forms a light field. There is a sharp demarcation between the light and dark fields. The telescope is moved until it is centered on this line.

The circular scale is not graduated in degrees, but directly in refractive indices, calculated as shown in equation (1). The prisms are jacketed, so that the temperature may be controlled to 0.2° with a stream of thermostated water.

Instead of using monochromatic light, white light is used, with a compensator of two sets of prisms, as described on page 330, which are rotated in opposite directions by the screw head at the side of the telescope tube.

The refractometer is connected to the water line from the thermostat. The prisms are opened like jaws after turning the lock nut to the right, and they are wiped with a soft cloth, care being taken not to scratch them. The prism jaws are closed and locked, and the liquid is introduced with a pipette into the hole at the side. The instrument is turned back until the telescope is in a convenient position, and the mirror is adjusted to reflect the light from a frosted electric lamp into the refractometer. The prism is rotated by means of the arm, until the border between the dark and light fields passes exactly through the intersection of the cross hairs.

If the border line is fringed with color, the compensator is rotated until the color disappears. If the boundary is not sharp and well defined, the mirror and lamp are adjusted until a distinct half-shadow is obtained. If the line or the cross hairs are blurred, the eyepiece is moved forward or backward until a good focus is obtained.

When the line of the half-shadow passes through the intersection of the cross hairs, the vernier is read to the fourth decimal place. The small eyepiece is adjusted to give a sharp focus on the scale.

The refractive indices of two or three liquids are determined, using at least one liquid that was measured also in the Pulfrich refractometer. The refractive indices of a mixture of liquids at different compositions are determined and plotted against the percentage compositions. By interpolation on this curve, an unknown composition may be easily determined from its refractive index. Nitrobenzene and toluene or some other high-boiling miscible pair of liquids may be used, the refractive index being determined for the pure liquids and for 25, 50, and 75 per cent mixtures, accurately weighed. Thorough mixing is essential. An unknown mixture of the two is then determined.

In addition to using the Abbe refractometer for analyzing a binary mixture it is used to illustrate the determination of the purity of a substance. A test tube is half-filled with benzene to which a few drops of carbon tetrachloride is added as an impurity. The refractive index is taken. The test tube is placed in an ice bath, and half the liquid is frozen. The mother liquor is decanted off and sucked up through a closely fitting tube provided with filter paper stretched across its lower end and tied with thread. The crystals are sucked as dry as possible, inverting the test tube for drainage, after which they are melted and

the refractive index is taken again. The liquid is chilled again until half of it is frozen, and the process is repeated until further purification by freezing gives no further change in refractive index.

The *immersion refractometer* is shown in Fig. 14. It is particularly convenient for analyzing solutions. Light hitting the face of the prism, at all angles up to the grazing angle, is refracted to give a light field. The sharp edge between the dark and light field is read directly on a transparent scale.

Three solutions of a salt (*e.g.*, sodium chloride or potassium chloride) are made up accurately with concentrations varying from 2 to 10 g in 100 g of water. The salt is dried first by heating it in an evaporating dish with a Bunsen burner and then drying in a desiccator. The solution must be mixed thoroughly by pouring back and forth into a beaker. The commonest source of error in an accurate measurement of this kind lies in incomplete mixing. Several small beakers, each containing a pure liquid or a solution, are set into the rack in the thermostat, care being taken to avoid flooding.

FIG. 14.—Immersion refractometer.

The refractometer is hung on the wire frame by means of the hooks near the eyepiece, so that the prism dips into the solution. The mirror is adjusted so that the light from the lamp, which is placed in front of and slightly above the bath, is reflected through the thermostat and beaker and into the refractometer. If the half-shadow is ill-defined, the mirror and lamp should be adjusted. The ring which encircles the barrel is turned until the compensator eliminates the color fringe.

The reading is taken by noting the position of the border line between the dark and light fields. The micrometer is set at zero when the scale is read. Fractions of a scale division are determined by turning the micrometer screw and scale until the edge of the shadow touches the nearest line on the scale.

Check readings are taken, and then the beakers are refilled for a second series of readings. Refractive index is plotted against composition, and from this graph the concentration of a solution of unknown concentration is determined.

The scale readings may be checked with Wagner's "Tables of Refractive Index."[4]   The tables are made for 17.5°C., and a correction for 25°C. is made by determining the scale reading for pure water at the two temperatures.

The scale readings may be converted into refractive indices by reference to Wagner's "Table."[4]   This conversion is unnecessary in analysis, when the concentrations of the known solutions are plotted directly against the scale readings.

Practical Applications.—Measurements of the indices of refraction of certain substances are of importance in physical chemistry.   They are helpful in identifying and establishing their purity, in determining the molecular structure of organic compounds, and in the quantitative analysis of certain types of solutions.   Each type of refractometer has its particular use.

The Pulfrich refractometer is very accurate, and it is extensively used in research.   It permits a calculation of the refractive index to about 2 parts in 100,000 over a wide range of refractivities.   By the use of additional prisms, of different refractive indices, the range may be increased.

The Abbe has a number of special applications, particularly in food analysis and in the testing of oils.   It covers a wide range of refractivities and uses but a very small amount of sample.   It is very convenient because it uses ordinary white light and gives the readings directly in refractive index.

The immersion refractometer is very sensitive over a narrow range of refractive index and is, therefore, well suited to the measurement of the refractive index of solutions.   This fact makes possible the quantitative analysis of solutions.   A refractometer with interchangeable prisms is now available, covering several different ranges.

Suggestions for Further Work.—Refractive indices of additional compounds and binary mixtures may be determined.   The refractive indices of solids may be determined, as described on page 332.   The refractive indices may be determined at different wave lengths, as described on page 332.

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11. Polarimetry

Experience is gained in the operation of the polariscope and its use for analytical purposes.

Theory.—When a beam of light is passed through Iceland spar, two beams are transmitted, each vibrating in a plane which is perpendicular to the other. A Nicol prism is composed of two sections of Iceland spar, so cut (and again sealed together with Canada balsam) that one of the rays is refracted to the side and absorbed so that all the light which passes through is vibrating in one plane only. According to the theory of optics, plane polarized light is made up of two components, right circularly polarized light and left circularly polarized light. When the plane polarized beam enters an optically active medium, there occurs the phenomenon of circular double refraction: either the left or the right circular component is preferentially decreased in velocity, depending on whether the medium is dextro- or levorotatory, and the two components on leaving the medium therefore combine to give polarized light in a plane that has been rotated with respect to the original beam.

Certain substances possess the power of rotating the plane of vibration. This phenomenon is observed in some gases and in many crystals, liquids, and solutions. In the case of crystals the rotation may be due to the arrangement of the atoms in the molecule (sugar) or it may be due to the lattice structure of the crystal (quartz). An asymmetric carbon atom can give rise to optical rotation. With such a carbon atom, each atom or radical attached to the carbon is different.

The magnitude of the optical rotation is measured with a polarimeter, which consists primarily of two Nicol prisms, between which the optically active substance is placed. When the second Nicol, known as the "analyzer," is placed at right angles to the first, no light can pass through, but when a substance that is capable of rotating the plane of polarized light is inserted between the Nicols, light can again be seen through the analyzer. The angle through which the analyzer must be turned to darken the field again is the measure of optical rotation. If the analyzer is turned clockwise to restore darkness, the substance is said to be dextrorotatory. If darkness reappears when the analyzer is turned counterclockwise, it is levorotatory. The angle could be read when the field is darkest but the error would be large. It is much better to compare the field with another field of nearly the same brightness, as is done in the half-shadow or triple-shadow polarimeter.

Apparatus.—Polarimeter; sodium-vapor lamp or other source of monochromatic light; sugar solutions.

Procedure.—The principle of the Landolt-Lippich triple-shadow polarimeter is illustrated in Fig. 15. Behind the large polarizing Nicol prism P are placed two auxiliary Nicols, set at a slightly different angle

of rotation with respect to the prism P.   The difference $\theta° - 0°$ may
be adjusted to optimum conditions which will depend on the intensity
of the light and the transparency of the liquid.   When the analyzer A
is turned so that it is at right angles with the main polarizing Nicol,
the central strip of the field, as viewed through the magnifying eye-
piece, is dark and the sides are lighter, as shown at I.   When the
analyzer is turned through the small angle $\theta° - 0°$ to cross with the
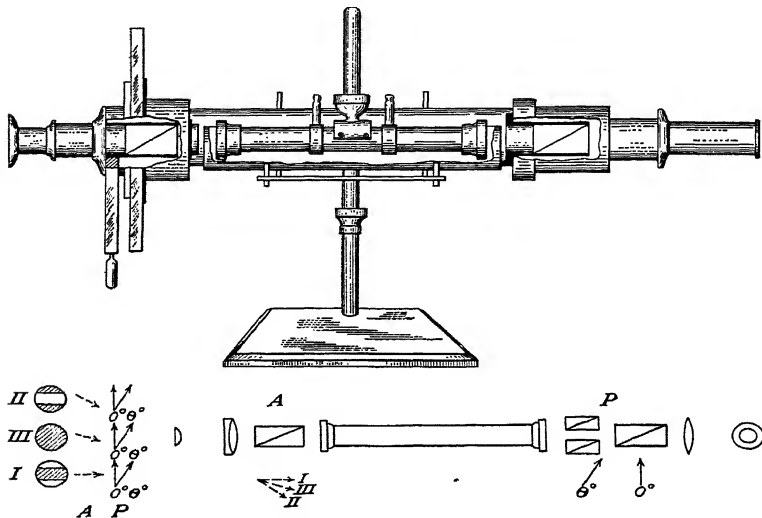
FIG. 15.—Polarimeter.

smaller Nicols, the sides are dark and the central strip is lighter, as
shown at II.   When the analyzing Nicol is turned back through half of
this small angle, it gives a uniform field as shown at III.   This proper
setting is readily found, and the corresponding reading of the scale is
recorded.   The scale is usually graduated directly into quarters of
degrees and, with the aid of verniers and a magnifying lens, the angles
may be read to 0.01°.

   The purpose of the experiment is to determine the specific rotation
of cane sugar.   Solutions of approximately 5, 10, and 15 g of sugar are
made up to volume in 100-ml volumetric flasks.   The crystallized
sucrose should be heated to 105°, cooled in a desiccator, and weighed
out accurately.

The solution is mixed thoroughly by pouring it from the filled volumetric flask into a clean dry beaker and back again, repeating the process several times. Inadequate mixing is the most common source of error in this experiment. The concentration of sugar in an unknown solution is determined by measuring the rotation.

Since the angle of rotation depends on the wave length of the light used, it is necessary to use a monochromatic light source for the polarimeter. The intense light of the sodium-vapor arc (page 393) is best, but a small crystal of rock salt or some fused sodium chloride on top of a Méker burner may be used. The green line of the mercury-vapor lamp at 5,461 Å is very satisfactory when used with a suitable filter (pages 392 and 395). Green light is often used in optical experiments because the eye is more sensitive to green than to other colors.

The light should be placed at a distance of about 20 cm from the end of the polarimeter, at the proper focal distance, and not close enough to heat the instrument.

The tube is rinsed and filled with distilled water, as full as possible, and the cap is screwed on, not tightly enough to cause strain as this would produce a rotation. Any small air bubble remaining is driven up into an enlargement, above the line of vision. The glass plates at the ends must be clean, and the exposed surface must be dry. The analyzer is rotated until the field is uniform, and several readings are taken on each side of the scale (0 and 180°). The averages give the right and left zero points. The setting of the analyzer should always be approached from the same direction in order to maintain identical mechanical conditions. These zero readings are subtracted from the readings on the optically active material. They should be taken at the beginning and end of each set of determinations.

The tube is next rinsed two or three times with the sugar solution and filled as before; three or more readings are taken on each of the two verniers. The difference between the average reading on the right and the zero on the right gives the rotation. Since, however, the circular scale may not be exactly centered, this rotation is averaged with the rotation read on the left-hand scale.

Alcohol, and also calcium chloride, may be added to another sugar solution before making up to the 100-ml mark in order to determine if the nature of the solvent is a factor in the rotation.

Calculations.—The optical rotations of the three different sugar solutions may be plotted against their concentrations, giving a calibration curve for sugar solutions. From this curve the concentration of a sugar solution of unknown concentration may be determined by interpolation.

The magnitude of the optical rotation is affected by the concentration, the length of the tube, the wave length of the light, and the temperature. To eliminate some of these variables, the specific rotation α for a given wave length at a given temperature is defined by the equation

$$[\alpha]_D^t \quad \frac{100\alpha}{}$$

where α = the observed angle of rotation.

    l = the length of tube in decimeters.

    c = the number of grams of material dissolved in 100 ml of solution.

    t = the temperature at which measurement is made.

    D = the line for sodium vapor (5,890 Å).

The tubes ordinarily used in work of this kind are exactly 2 dm in length. Longer or shorter tubes are available. The product of the molecular weight and the specific rotation gives the molar rotation. Sometimes this quantity is divided by 100 to get units of more convenient size.

The specific rotation should be compared with accepted values given in tables. The concentration of the sugar solution of unknown concentration is determined by substitution in the formula for the specific rotation, and checked by interpolation on the graph.

When the density d and the grams per 100 g of solution p are known, the concentration c in the formula may be replaced by pd.

Practical Applications.—Optical rotation is used in identifying materials and in determining the structure of organic compounds. It finds important applications in quantitative analysis, as, for example, in the determination of the concentration of sugar in solution. Certain chemical changes may be followed without disturbing the system, as, for example, in the rate of inversion of cane sugar by catalysts (described on page 161).

Suggestions for Further Work.—Other substances such as tartaric acid or camphor, which are optically active, may be studied in the same manner as sugar. Nonaqueous solutions may be used, such, for example, as camphor in benzene, carbon tetrachloride, and acetone. The influence of solvent on the optical rotation of the solute has not yet found quantitative expression.

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12. Colorimetry

Theory.—A colorimeter is an instrument by means of which the concentration of a solution is determined by the intensity of the light transmitted through it. This determination is made by a comparison with standard solutions of known concentration. The constituent to be determined in an analysis is caused to form a compound (if it is not already colored), which gives a distinctly colored solution. The intensity of this coloration is approximately proportional to the concentration, provided that the solution is sufficiently dilute. If the intensity of color of the solution of unknown concentration is compared with that of a standard, the concentration of the former may be determined. This comparison may be accomplished in two different ways:

1. By altering the depths of the two columns of liquid until the light transmitted through each is of equal intensity. At this position, the concentrations of the two solutions are inversely proportional to the depths, which are read directly from the instrument.

2. By bringing the intensity of color of the two solutions to an exact match by looking through equal thicknesses and diluting one to a measured extent until the match is obtained.

The method of procedure to be followed in this experiment is that of altering the depths of the two columns of liquid until the balance point is reached. It may readily be shown from Beer's law that, when the two halves of the field in the colorimeter show the same color and intensity, the concentrations of the two solutions are inversely proportional to the depths of the columns of the two solutions.

According to Lambert's law, successive layers of a given thickness of a uniform medium absorb the same fraction of incident light. According to Beer's law, equal increments in the concentration of dissolved material in a transparent solvent absorb the same fraction of incident light. Combining these two laws and expressing them mathematically,

$$\frac{I}{I_0} = e^{-kcd}$$

where k = the absorption coefficient, for a given color.
c = the concentration of solution.
d = the depth of solution.

I_0 = the intensity of incident light.

I = the intensity of light at depth d.

In the colorimeter the incident light intensity is the same, and the depths are adjusted so that the transmitted light intensities are the same. Therefore I_0 and I are the same for both tubes and

$$\frac{I}{I_0} = e^{-kc_sd_s}$$

for the standard solution, and

$$\frac{I}{I_0} = e^{-kc_xd_x}$$

FIG. 16.—Colorimeter.

for the solution of unknown concentration x. Therefore, when the intensities are matched,

$$kc_sd_s = kc_xd_x$$

Since k is the same for all solutions of the same solute in the same solvent,

$$c_sd_s = c_xd_x, \qquad \text{or} \qquad \overline{d_x}$$

The unknown concentration c_x, then, is determined from a knowledge of the two depths and the concentration of the standard solution.

If the standard solution is kept at a fixed depth, it is evident that the depth of the unknown solution required to give a match in the colorimeter is inversely proportional to the concentration.

Apparatus.—Colorimeter; potassium permanganate, copper sulfate, and other colored salts or dyes.

Procedure.—The Duboscq colorimeter is shown in Fig. 16. Diffuse daylight, or light from a frosted electric light (or better, from a special illuminator), is reflected from the mirror or white surface up through the two colorimeter tubes. The light is then reflected so that the two beams appear side by side in the eyepiece. The standard solution is first placed in both tubes with the same setting, and the colorimeter and light are turned so that the two halves of the field are of equal brightness. If the instrument has two mirrors, this adjustment is facilitated.
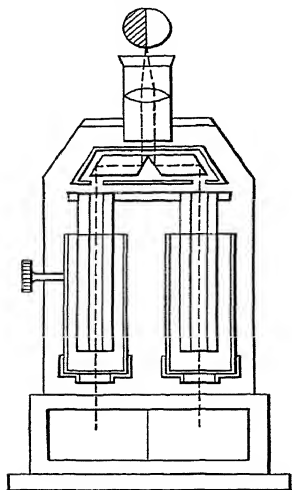
After this adjustment the instrument should not be moved from its position during the course of the experiment.

The method of analysis may be illustrated by the following procedure, using potassium permanganate solutions. A 0.01 per cent solution, prepared by dilution from a stock of 1 per cent solution, forms a convenient standard. A small quantity of this solution is placed in the cup designed to receive the standard, and the depth is adjusted to a definite position, preferably an exact number of millimeters.

The other cup is filled with solutions obtained by diluting some of the standard solution to 0.009, 0.008, 0.007, 0.006, etc., per cent potassium permanganate, and the plunger is adjusted to give an exact match in the colorimeter field. The depth is then read on the vernier scale. The solutions are prepared by diluting with the required amount of water.

For accurate results in colorimetry, solutions whose concentrations are of the same order of magnitude should be compared, otherwise the color tints are difficult to compare as to intensity. Therefore, for solutions more dilute than those of the first series, a new standard of comparison is to be used. This standard of comparison may well be a 0.005 per cent solution, obtained by dilution from the previous standard solution. Proceeding in an exactly similar manner, solutions of 0.005, 0.0045, 0.0040, 0.0035, and 0.0030 per cent may be successively analyzed, constituting a second series of determinations.

At each concentration, one set of readings should be made with the plunger in the standard solution at a fixed depth, *e.g.*, 2 mm, to facilitate a later calculation.

In a study of the colorimeter, it is desirable to have practice in comparing solutions of various colors; so the experimental work should not be limited to the study of a single substance.

Calculations.—It has been shown that, when the two halves of the field have the same color and intensity, the concentrations of the two solutions are inversely proportional to the depths of the columns of the two solutions. When this relationship is used, the concentrations of the solutions in the several series of measurements are calculated from the observed depths and checked against the concentration as calculated from the dilution.

The plunger readings obtained with the standard plunger at a fixed depth (2 mm) are plotted against the concentrations. What type of curve is obtained?

Practical Applications.—The colorimeter is an instrument of great practical importance in that it has displaced many laborious methods of quantitative analysis, both as a timesaver and as a more accurate method. As a timesaver, it is

frequently used with some sacrifice of accuracy. As a more accurate method, it is used for the determination of small amounts of substances that do not lend themselves readily to the methods of gravimetric or volumetric analysis.

The colorimeter is used successfully in many industries. In steel analysis, titanium, manganese, and carbon are readily determined. In metallurgy, small amounts of aluminum, copper, gold, lead, iron, bismuth, and other metals are determined. Hydrogen-ion concentrations are easily measured.

It also finds extensive application in biological and medical laboratories. A special type of colorimeter, known as the "hemoglobinometer," is used to determine the percentage of hemoglobin in the blood.

Suggestions for Further Work.—Some colorimeters are readily converted into nephelometers, by means of special attachments supplied by the manufacturers, using lateral illumination. Nephelometers make use of the fact that light which strikes particles suspended in a liquid will be scattered and a portion will be reflected into the observation tube, and that the brightness of the field will be determined by the number of the particles reflecting the light. Comparisons between solutions of known and unknown turbidity may then be made, in a manner similar to that used in a colorimetric comparison. Various suspensions, such as silver chloride (determination of chlorine in water) and barium sulfate (determination of sulfur in a fuel), may be studied for advanced work.

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13. Photoelectric Colorimetry

In this experiment solutions are analyzed quantitatively by the amount of transmitted light, which is measured by a light-sensitive electrical instrument.

Theory.—The concentration of a colored material in solution may be readily determined by the amount of light that is absorbed. Such success has been made in the electrical measurement of light intensity that photoelectric colorimeters are rapidly displacing colorimeters in which the intensity of color of the solution and that of the standard solution are matched by eye.

The fundamental equation of colorimetry and photoelectric colorimetry and, in fact, of all phenomena involving the transmission of

light is the Lambert-Beer's law

$$= I_0 e^{-kdc} \tag{1}$$

where I_0 = the intensity of incident light.

I = the intensity of transmitted light.

c = the concentration, best expressed in moles per liter.

e = the base of the natural logarithms.

The thickness d is constant when the measurements are carried out in a cell of fixed dimensions. The constant k depends on the nature of the particular absorbing material. Under these conditions the concentration is easily calculated from an experimental determination of the fraction of light transmitted.

One of the simplest ways of calculating the concentration of a dissolved solute from the absorption of light is to plot the logarithm of the fraction of light transmitted I/I_0 against the concentration c. A straight line should result, provided that (*a*) the light is nearly monochromatic; (*b*) the colored material absorbs only this light; and (*c*) the nature of the absorbing material remains unchanged on dilution; *i.e.*, it does not ionize, dissociate, or combine with the solvent in such a way as to change the color.

It is advantageous for both theoretical and practical work to plot log I/I_0 against concentration. If the line is straight, the conditions are such that Beer's law applies and the concentration of the material in solution can be calculated very simply from the transmission by using the formula

$$c = \frac{2.303}{kd} \log \frac{I_0}{I} \tag{2}$$

The constant k is determined from the slope of the straight line.

If the absolute value of the constant k is not necessary and only an empirical method for analysis is needed, graphical interpolation on this plot will be sufficient, even though the line is not straight. If the conditions are kept the same and the range of wave lengths is not changed, the curve will be reproducible and reliable. In general, the line will not be straight if white light is used because the Beer's constant k is different for different wave lengths. In fact, part of the white light will pass through a colored substance with very little absorption, and it will be registered on the measuring instrument without regard to changes in the concentration of the solute. Changes in the intensity of light of a small range of wave lengths may go undetected in the presence of intense light in other parts of the spectrum. In colorimetry the eye can pick out a single color more easily.

The photoelectric colorimeter can be used much more effectively if the light is nearly monochromatic and of such wave length as to be selectively absorbed by the colored material. The chief requirements for a successful instrument are (*a*) a constant source of light sufficiently intense throughout the range of wave lengths desired; (*b*) means of obtaining light within a narrow range of wave lengths; and (*c*) a sensitive instrument for measuring accurately the intensity of light, even though it is weak.

The tungsten filament is usually used as the source of light operating at low voltage and high amperage. Constancy of light is obtained by the use of storage batteries, a special transformer with high reactance running at an overload, an electronic relay voltage controller, or a dynamo driven by a synchronous motor. For green and blue light a mercury arc may be used.

The requirement for constant intensity may be rendered unnecessary by splitting the light into two beams with mirrors or biprisms and passing one through the solution and the other through the solvent. Since the difference in intensity of the two beams is measured rather than the absolute intensities, a fluctuation in the intensity of the lamp is not serious.

For obtaining monochromatic light, filters are cheapest and are usually adequate for analytical purposes. A set of four or five or more is necessary so that a suitable one may be selected for solutes of different color. A monochromator, in which the light is spread out into its wave lengths by means of a prism or special grating, is better, provided that the instrument for measuring the intensity is sufficiently sensitive to permit the use of a narrow range of wave lengths. A more complete discussion of monochromators is given on page 397.

The transmitted light may be measured in several different ways. A thermopile with a sensitive galvanometer is equally sensitive in all parts of the spectrum, but ordinarily it is not sufficiently sensitive to use with a tungsten lamp, particularly in the blue. The barrier-layer cell, one example of which is the photronic cell, is simple and effective. It generates an electromotive force which is easily measured by a galvanometer or microammeter, but it may show a drift and a fatigue on long exposure to bright light. The photoelectric cell with suitable amplifiers is the most sensitive measuring apparatus, but unless carefully designed and screened the amplifying circuit may give trouble.

Apparatus.—Photoelectric colorimeter with light filters or monochromator, and light-sensitive cell for measuring intensities; absoption cell; colored solutions such as cupric salt, ferric salt with salicylic acid, potassium permanganate, hemoglobin, chlorophyll.

Procedure.—The intensity of light transmitted by a colored solution and by the pure solvent is determined at several different dilutions for two or more colored substances. The exact procedure will depend on the particular type of photoelectric colorimeter used. The directions supplied by the manufacturer should be followed.

If a photoelectric colorimeter is not available, it is possible to make one by using a photocell and galvanometer, or an electrical exposuremeter such as is used in photography to which is attached a millimeter scale. An automobile headlight and storage battery or step-down
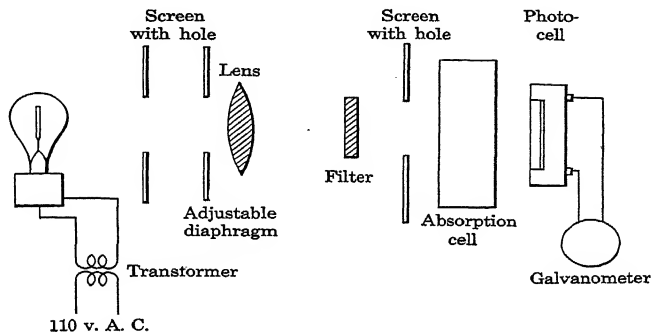
FIG. 17.—Photoelectric colorimeter.

transformer, three or four filters of glass (page 395), and an absorption cell complete the equipment as shown in Fig. 17. Corning signal red filter No. 243 will exclude all light except red. Excellent monochromatic light in restricted regions of the spectrum may be obtained with an inexpensive mercury-vapor lamp (page 392) with filters: green light at 5,460 Å with Corning filters 350, 430, and 512 in series; blue light at 4,360 Å with filters 038 and 511; ultraviolet light at 3,650 Å with filters 586 and 738. The absorption cells 1 or 2 cm thick are made from flat glass or from a short length of glass tubing provided with a side arm and glass windows. Microscope slides make good material for cells. The windows may be attached with water glass for nonaqueous solutions or with sealing wax or cement covered with melted paraffin for aqueous solutions. Two identical cells are used, one for the solution and one for the solvent. The lens is adjusted so that the light which covers the photocell is nearly uniform.

A filter is selected that will transmit only the light which is absorbed by the solute. If the absorption band of the solute is narrow, a selec-

tive filter giving only a limited range of wave lengths is necessary. It can be chosen by viewing the absorption of both with a spectroscope, or more simply by holding the various filters between the solution and the eye. That filter which makes the solution look darkest will give the greatest spread between the readings for the concentrated and dilute solutions and is the one to be selected. The filter giving the lowest transmission reading is generally the best. If a monochromator is used, the instrument is turned to give the wave-length region that coincides with the absorption band.

The absorption cells must be filled full enough so that the meniscus at the top is well above the path of the light. They must be scrupulously cleaned, using sulfuric acid and dichromate solution unless this solution attacks the cement. Pyrex cells with fused-on windows or specially manufactured cells are best. In some cases test tubes may be used. The two cells, one for solvent and one for solution, are checked by obtaining the amount of light transmitted through the same solution or solvent. The deflections should be the same; if they are not, other cells should be tested until a suitable "pair" is found.

In all photoelectric colorimeters, arrangements are made so that the percentage of light transmitted through the solution can be read directly or calculated easily. In one type an iris diaphragm, similar to that used on cameras, is used to reduce the intensity of light by reducing the area. It is set so that the full scale swing to 100 on the galvanometer is obtained with the pure solvent. Then the lesser deflection obtained when the solution is used gives a direct measure of the percentage of light transmitted. Since the photocell is subject to fatigue and the lamp may change in intensity, frequent adjustments may be necessary to keep the light transmitted by the solvent at 100. In other types a potentiometer arrangement is used in which resistances are changed by turning dials in such a way as to keep the galvanometer on zero. The potential as measured by the markings on the dials is proportional to the intensity of light. In still other types, electron-tube circuits and resistance dials are used to measure the change in resistance of a photoelectric cell produced by light.

After practicing with the photoelectric colorimeter on colored solutions until checks can be readily obtained, a study is made of the relation between concentration and transmission of light. The concentrations are adjusted to cover a range from approximately 90 to 10 per cent absorption, the lower concentrations being obtained by diluting the more concentrated solution successively with the solvent.

A dark-colored solution of known concentration is diluted with measured volumes of the solvent until about 10 per cent of the light is transmitted as measured in the photoelectric colorimeter. Then the solution is diluted successively, each time with an equal volume of solvent giving ½, ¼, ⅛, etc., concentration, until the transmitted light is about 90 per cent of the incident light.

Two or more of the following solutions may be used. Other colored solutions may also be used, a suitable filter being selected in each case.

1. Copper sulfate solution to which has been added an excess of ammonium hydroxide, using a red filter.[5]

2. Iodine with starch, using Corning red shade yellow No. 348.[6]

3. Potassium permanganate, using a green filter.[5]

4. Ferric chloride, using a green filter.

5. A dilute solution of hemoglobin or blood,[7] using a blue filter. The carboxyhemoglobin, produced by bubbling through carbon dioxide, has a deeper red color.

6. Chlorophyll in acetone, extracted from green leaves with acetone, using a red filter.

A blue filter may be used also on a different absorption band.

7. Titanium sulfate with sulfuric acid and hydrogen peroxide, using a blue filter.

Calculations.—For each solution studied, a graph is prepared in which $\log I/I_0$ is plotted against the concentration in moles per liter, or in other suitable units. Semi-log paper is convenient for this work. If the line is straight, Beer's law is seen to apply, but if the range of wave lengths transmitted by the filter or monochromator is wider than the range absorbed in solution, the line may not be straight. The curved line is used almost as easily as the straight line for interpolation and finding the concentration of an unknown solution.

Practical Applications.—There have been few instruments that have developed as rapidly as the photoelectric colorimeter and that have found in a few years so many applications in analytical chemistry.[1-4] It is used for analyses not only by absorption of light but by emission of fluorescence, as for example in the case of riboflavine[8] and chlorophyll.

Suggestions for Further Work.—Among the many substances that may be analyzed are vitamins,[2,9] carotene,[10] sulfanilimide,[11] ammonia with Nessler's reagent, nitrites[12] with Griess' reagent, and phosphorus in steel.[13]

The photoelectric colorimeter may be used also as a nephelometer, following the opacity of a suspended and finely divided precipitate by the intensity of transmitted light. Silver chloride, lead sulfide, and barium sulfate are examples.

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14. Spectrophotometry

This experiment requires a spectrophotometer, several types of which have been developed recently. It is used to map spectra and to analyze one or more colored substances in solution.

Theory.—The spectrophotometer combines the features of the spectroscope (page 39) and the photoelectric colorimeter (page 58). In other words it separates the light into separate regions by refraction or diffraction and measures the intensity in each region. It does what a photoelectric colorimeter would do if it could be provided with a continuous set of practically perfect filters. The light is spread out into a spectrum by a prism or a diffraction grating. Improved gratings are now made with the lines ruled at a definite angle so as to throw most of the light into the first-order spectrum, thus increasing the energy available and improving the purity. The purest light is obtained with a double monochromator with two prisms or gratings. For example, if 5 per cent of the light is scattered by the first prism, then, theoretically, 5 per cent of 5 per cent, or 0.25 per cent, of the light passing the second prism and slit will fall outside the selected range of wave lengths.

In order to make the light monochromatic in this way the intensity is greatly reduced, and only recently have instruments, in which the energy is measured directly by electrical means, become available for general laboratory use. Photoelectric cells and amplifying circuits

are used in some types. In others a barrier-layer cell and sensitive galvanometer are used. A thermopile with its nonselective radiation absorption constitutes the best receiver of energy, but a galvanometer of very great sensitivity is then necessary.

For absorption spectra the beam of light is sometimes split up into two beams, one going through the absorbing medium and the other going through some device for reducing the light by definite measured increments. The intensity of this beam of light may be reduced (*a*) by a sector wheel, in which a revolving wheel is provided with adjustable slots, (*b*) through Nicol prisms which are partially crossed to give the necessary intensity, or (*c*) by passing through a wedge of nonselective absorbing material which absorbs varying amounts of light. After passing through the spectrophotometer the two beams are brought to adjacent positions on each part of the spectrum, where they are viewed with the eye, photographed on a plate (page 294), or measured with a photocell. The type that directly measures the transmitted light by electrical means is gaining rapidly in popularity, and several excellent makes are now available. One of the first successful instruments utilizing a photoelectric cell was described by Zcheile, Hogness, and Young.[1]

The advantage of a sensitive spectrophotometer is obvious. The complete spectrum is quickly obtained with percentage transmissions at each wave length. The true color of a material or solution may be defined in quantitative terms. The bands of maximum absorption are quickly found, and then the spectrophotometer with a narrow slit is set directly on this absorption band for a series of measurements at different dilutions. Under these conditions a plot of log I/I_0 against concentration should be straight unless association or dissociation of the solute or combination with the solvent is involved—at least the departure from a straight line is not likely to be due to a failure to match the absorption band with an inadequate filter.

Special graph papers, with percentages to 100 plotted vertically against wave length, and semi-log paper suitable for plotting Beer's law curves can be purchased.

The spectrophotometer can be used in the ultraviolet and infrared as well as in the visible regions of the spectrum. Powerful tungsten lamps, corex cells and optical parts, and sensitive photocells enable one to go to 3,000 Å. In the infrared, optical parts of sodium chloride permit an extension to 15 μ and potassium bromide will go to 25 μ. More materials are colored in the ultraviolet than in the visible, and in the infrared almost all substances are colored. In fact, there are so many overlapping absorption bands in the infrared that analysis by the

spectrometer is difficult.   A thermopile must be used for measuring the intensity of transmitted light in the infrared.

Apparatus.—Spectrophotometer; didymium glass; solutions of potassium permanganate, and potassium dichromate; colored solutions as described on page 63; copper sulfate or ferric sulfocyanate.

Procedure.—The absorption spectrum is determined by turning the instrument gradually and determining the transmission at the different wave lengths.   Readings may be taken every 300 or 400 Å, except that in the region of an absorption band more frequent measurements are necessary.   It is a good plan to plot the transmission directly on a graph as soon as read.   If there is a large gap that is uncertain, more readings can then be taken at once.   The instrument should always be turned in the same direction just before a reading to prevent error from a "slack" in the bearings.

Didymium glass (Corning filter No. 512) is conveniently used for testing the dispersion of a spectrophotometer or a spectrograph because it has several narrow absorption bands which are well known. The spectrum of this glass or of a dilute solution of potassium permanganate solution (0.01 per cent) is determined.

The color of some common material is described quantitatively by determining its absorption spectrum and plotting the percentage transmission at the different wave lengths.   A dilute solution of ink, blood, paint, or an acetone extract of chlorophyll, a flower petal, or a food material may be used.   Colored glass filters may be checked.

A calibration curve is drawn for at least one of the substances described on page 63, and an "unknown" sample of the material is determined by interpolation on the line.

The emission spectrum of a mercury vapor lamp is plotted.   The H4 lamp (page 392) is convenient.

Colorless or slightly colored salts in solution can often be made intensely colored by the addition of certain organic compounds.   To illustrate this, a solution of potassium dichromate may be run through with the spectrophotometer.   Then a little diphenyl carbazide is added to a very dilute solution ($10^{-5} M$), and a different and more intense color is produced.   The spectrum of this solution is plotted. The absorption at 5,000 Å follows Beer's law and is suitable for accurate analysis.

Two or more colored substances may be analyzed in the same solution if their absorption bands are separated sufficiently and there is very little overlapping.

It is possible to determine equilibria in solution if the reactant and product have different colors.   Graphs showing $\log I/I_0$ plotted against concentration are prepared for ferric ion with dilute hydro-

chloric acid (to prevent hydrolysis) and for the deep red $FeCNS^{++}$ of ferric thiocyanate containing an excess of potassium thiocyanate.[2] Then the concentration of each in solutions containing different ratios of Fe^{+++} and CNS^- is determined by setting the spectrophotometer at a definite absorption band for each. An equilibrium may be calculated. Other equilibria that may be studied in this way are iodine and the tri-iodide ion formed in a solution of potassium iodide, or iodine chloride formed from iodine and chlorine in a solution of carbon tetrachloride.

Practical Applications.—Almost any of the spectrographic or colorimetric determinations listed on pages 41, 57, or 63 may be done better with the spectrophotometer.

The color of nearly any commercial product can be described quantitatively with the spectrophotometer and checked for uniformity.

The spectrophotometer and the photoelectric colorimeter can be used for the determination of traces of mercury, benzene, and other organic vapors in air by the measured absorption of ultraviolet light.[4]

Suggestions for Further Work.—Suggestions are given on pages 43, 58, and 63.

An interesting equilibrium constant has been determined for the association of the ions of methylene blue and of thionine, using a spectrophotometer. The monomer of methylene blue absorbs at 6,565 Å and the dimer at 6,000 Å. Beer's law is not followed on account of this association. The equilibrium constant is determined by extrapolating the extinction coefficient to infinite dilution as described by Rabinowitch and Epstein.[2]

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CHAPTER IV

SOLUTIONS

15. Elevation of the Boiling Point

The boiling points of a solution and the pure solvent are determined and used for calculating the molecular weight of the nonvolatile solute.

Theory.—When a nonvolatile solute is dissolved in a solvent, the vapor pressure of the latter is decreased; as a consequence, the boiling point of the solution is higher than that of the solvent. The extent of the elevation depends on the concentration; if a mole of solute is dissolved in 1,000 g of solvent, the boiling point is raised K_b deg. Also, if g grams is dissolved in G grams of solvent, the boiling point is raised ΔT_b deg. Then the molecular weight M of the solute is obtained from the following equation:

$$M = \frac{1,000 K_b g}{G \Delta T_b} \tag{1}$$

The constant K_b is characteristic for any liquid. It is called the "boiling-point constant" or "molal elevation."

In order to determine the boiling temperature of a solution, the thermometer must be immersed in the solution (not in the vapor, as in the case of a pure liquid), and it becomes particularly important to eliminate superheating. This source of error may be eliminated by passing vapor into the solution and condensing it so that the heat of condensation raises the solution up to its boiling point. Radiation and conduction from a body at a high temperature is eliminated, and the vapor cannot cause superheating. Superheating may be eliminated also by electrical heating (page 316).

Apparatus.—Boiling-point apparatus of the Cottrell type; Beckmann thermometer or other thermometer reading to 0.01°; pure benzene, acetone, benzoic acid.

Procedure.—A boiling-point apparatus of the Cottrell type [1-4] is shown in Fig. 18. A weighed quantity of the solvent is placed in the tube sufficient to come a centimeter or so below the thermometer bulb, and a Beckmann thermometer or other thermometer reading to 0.01°

is inserted in the cork. The apparatus is mounted vertically with clamps and heated with a small gas flame. If necessary, a cylinder of asbestos or metal is placed around the flame to keep drafts of air away. The purpose of the small inverted funnel, which is set up from the bottom on little projections, is to catch the bubbles of vapor and let them rise through the center tube and three vertical tubes. As
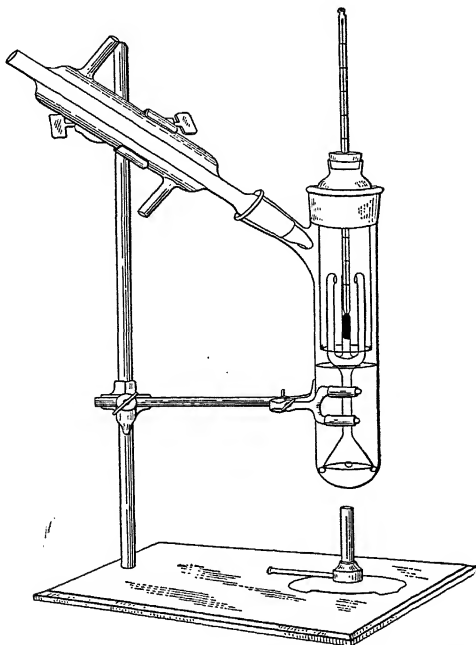
FIG. 18.—Modified Cottrell apparatus for determining the boiling point of a solution.

they discharge through these outlets they direct three sprays of liquid and vapor against the thermometer; any superheated solution comes to full equilibrium with the vapor by the time that it gets to the thermometer bulb.

The apparatus shown in Fig. 18 can be purchased with the Brown condenser, which contains a little pocket at its lower end that can be filled with condensed liquid by rotating the condenser through 180 deg. For experiments on the distillation of binary mixtures, the con-

denser is turned so as to catch samples, the condenser is then removed, and the sample is poured out for analysis. In the present experiment with a nonvolatile solute this feature is not used, and the condenser outlet is turned downward as shown, so as not to collect samples of the condensed vapor.

The elevation of the boiling point by benzoic acid is determined in a polar and a nonpolar solvent, and the molecular weight in each is calculated.

Acetone or alcohol is used first, and the boiling point of the pure solvent is determined. The quantity introduced is weighed to 0.1 g. If the liquid does not pump vigorously over the thermometer bulb, the level of liquid or the rate of heating is changed. If the boiling point is not constant, it may be necessary to redistill the liquid in an efficient fractionating column. The thermometer should be tapped just before a reading. The boiling point is quite sensitive to changes in pressure, and the barometer should be read and recorded several times during an extended experiment.

After the boiling point of the pure solvent has been determined, a weighed pellet of benzoic acid is introduced after first turning the burner off and allowing the liquid to cool before removing the condenser. The concentration should be such as to give a 1 to 5 per cent solution. To prevent loss of benzoic acid, it is pressed out in a screw-pellet machine before weighing, or it is packed into a short glass tube and rammed tight with a central rod acting as a plunger.

A second determination may be made in a more concentrated solution by adding a second pellet of benzoic acid.

The steady boiling point of the solution is determined in the manner already described. The determinations on solvent and corresponding solution should follow one another closely so as to minimize the effect of barometer changes.

The boiling point of pure benzene or carbon tetrachloride is determined, and then the flame is turned off and the liquid cooled while the condenser is removed and a pellet of benzoic acid introduced. The boiling point of the solution is then determined as soon as convenient.

Calculations.—The molecular weight is calculated by means of equation (1), using the constants for K_b shown in the following table. The pressure corrections for K_b, shown in the last column, may be neglected, unless the barometer is considerably below 760 mm.

Any variations from the theoretical value for the molecular weights are noted and explained. The percentage error in the determinations is calculated, wherever such procedure is justified.

Molal Boiling-point Constants[7]

Solvent	Boiling point at 760 mm	Molal boiling-point constant K_b	$\Delta P(\text{mm})$
Acetone........	56.0	1.71	0.0004
Benzene.......	80.2	2.53	0.0007
Bromo benzene	155.8	6.20	0.0016
Chloroform....	60.2	3.63	0.0009
Ethanol.......	78.3	1.22	0.0003
Ethyl ether....	34.4	2.02	0.0005
Methanol.....	64.7	0.83	0.0002
Water........	100.0	0.51	0.0001

Practical Applications.—Many materials cannot be vaporized, for direct determinations of the vapor density, without decomposition. In such cases the material is dissolved in a suitable solvent, and the elevation of the boiling point furnishes a rapid and convenient method for determining the molecular weight. Molecular weights of substances in solution are often different from the values found from vapor-density measurements.

The boiling points of solutions may be calculated with the help of equation (1) when the molecular weight of the solute is known.

Suggestions for Further Work.—The largest experimental errors are due to barometer fluctuations or an appreciable loss of solvent in the vapor and condenser. The first difficulty may be met by making corrections for pressure or by using two sets of apparatus at the same time, one for solvent and one for solution. The second difficulty may be met by analyzing the solution after the determination of the boiling point. A sample is withdrawn with a pipette and weighed in a weighing bottle. The solvent is then evaporated off in a current of air and the residue is
d.

The determinations of molecular weight may be made at three or more concentrations, and the values are extrapolated to infinite dilution. Only in this way can a reliable value for the molecular weight be obtained.[6]

The molecular weights of several different organic solids or liquids may be obtained, such as urea, naphthalene, oxalic acid, or sugar. Water may be used as the solvent in some cases, particularly with electrolytes.

A solvent, such as carbon tetrachloride, is used, for which the value of K_b is not given. The constant K_b may be determined by experiment with solutes of known molecular weight, or by thermodynamical calculation from the heat of vaporization per gram l and the boiling point T_b in absolute temperature, according to the following relation:

$$= \frac{0.002 T_b^2}{l} \tag{2}$$

A more elaborate and more accurate method may be used in which a thermocouple gives directly the difference in boiling point between the solvent and solution in two separate vessels.[8]

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16. Depression of the Freezing Point

The lowering of the freezing point constitutes one of the simplest and most accurate means of determining quantitatively the influence of a solute on the solvent. It is of practical value and is important in theoretical studies of solution. A study is made of a strong electrolyte, a weak electrolyte, and a partly dissociated electrolyte.
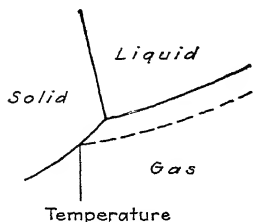
FIG. 19.—Freezing point diagram. Pressure-temperature diagram showing why a solute lowers the freezing point. The

Theory.—The addition of a solute to a liquid decreases the tendency of the solvent molecules to escape into the gas phase, *i.e.*, it lowers the vapor pressure of the solvent. If the solute itself is nonvolatile, the total vapor pressure of the solution is lowered. When the vapor pressure of the solution is lowered, the temperature of freezing is also lowered, because the vapor-pressure curve of the solution intersects the sublimation curve of the solid at a lower temperature as shown in Fig. 19. The solid phase (ice, in the case of water) separates when the temperature is lowered to a point where the vapor pressure of the solvent in the solution is just slightly greater than the sublimation pressure of the solid. The extent of the freezing-point depression depends on the concentration, and the following quantitative relation has been found:

$$M = \frac{1,000 K_f g}{G \Delta T_f} \tag{1}$$

In this equation, M is the molecular weight of the solute, and ΔT_f is the observed depression of the freezing point caused by the addition of g grams of solute to G grams of solvent. A constant K_f is called the freezing-point constant, or molal depression. It is characteristic of the solvent and corresponds to the depression produced by a gram molecule of solute dissolved in 1,000 g of solvent.

In case the solute dissociates into ions, each ion acts to lower the freezing point, and the freezing-point depression is increased. If it is assumed for weak electrolytes that the magnitude of this increase is a measure of the degree of dissociation α of the solute, the following formula may be applied:

$$\alpha = \frac{M_0 - M}{M(n - 1)} \qquad (2)$$

In this formula, M_0 is the theoretical molecular weight calculated from the sum of the atomic weights, M is the molecular weight actually calculated from the freezing-point depression, and n is a number, 2 or 3 or 4, giving the number of ions into which the molecule dissociates.

This formula is based on the classical theory of Arrhenius, according to which electrolytes are only partially broken up into ions. It is satisfactory for weak electrolytes but unsatisfactory for strong electrolytes. According to the more modern interpretation of the Milner-Debye theory, the strong electrolytes such as potassium chloride are really completely dissociated in aqueous solution; the molal freezing-point depressions are not exactly two, three, or four times the normal depression at finite concentrations, but considerably less, because of electrical interactions among the ions. These deviations from the behavior of ideal solutions are the result of mutual attraction of oppositely charged ions and the mutual repulsion of ions of the same charge. The properties of these solutions of strong electrolytes approach those of an ideal solution at extremely low concentrations.

The separation of pure solvent in the solid form increases the concentration of the remaining solution, and this increase may be considerable, particularly if the solution has been much supercooled. The best results are obtained by determining the concentration of the solution which is in actual equilibrium with the solid phase at the temperature recorded. Satisfactory results can be obtained, however, by weighing out solute and solvent to give a known initial concentration, provided that the temperature recorded is that at which the first bit of solid phase appears and remains small in amount. If considerable solid appears, it should be made to melt until only a small portion remains in equilibrium with the solution.

Apparatus.—Vacuum bottle with cork and ring stirrer; freezing-point thermometer ($+0.1$ to $-1.00°$ graduated to $0.01°$) or Beckmann thermometer; 10-ml weighing bottle; burette; 10-ml pipette; approximately $0.25N$ solutions of hydrochloric acid, acetic acid, monochloroacetic acid; 1 liter $0.1N$ sodium hydroxide.

Procedure.—A small vacuum bottle (1 pt.) is provided with a cork, through which passes the $0.01°$ thermometer and a ring stirrer as

Fig. 20.—Determination of the freezing point of a solution using a vacuum bottle.

shown in Fig. 20. The ring must be of such size and so placed that it cannot touch and break the thermometer bulb. The bottle is filled about one-fourth full with distilled water which has been chilled in an ice bath, and an equal volume of pure cracked or finely divided ice is added. The pieces of ice in a clean beaker are rinsed two or three times by decantation with distilled water in order to remove any electrolytes introduced from the melted ice. The rinsing water itself is cooled nearly to zero in order to prevent the melting of more ice which might introduce additional impurities.

If the ice is not pure, the freezing point of the ice bath will decrease as more and more of the ice becomes melted. If this decrease is enough to interfere with the accuracy of the experiments, it will be necessary to prepare pure ice by freezing distilled water in an electric refrigerator or in a salt and ice bath.

The ice and water in the bottle are stirred vigorously until a steady temperature is attained. Thermometers reading from $+0.1$ to $-1.0°$ are very convenient for aqueous solutions. The thermometer is tapped gently just before reading. If a Beckmann thermometer is used, it is adjusted so that the mercury comes near the top of the scale at the freezing point of the pure solvent. It is set in the manner described on page 422 (under supervision).

The water is drained off and replaced with a chilled solution of hydrochloric acid, about $0.25N$. The solution and ice are stirred thoroughly until a constant temperature is reached, whereupon the

thermometer temperature is recorded and a sample is removed, with a 10-ml pipette which has a piece of filter paper tied over its tip to prevent sucking in little pieces of ice. Since the weight of solute per 1,000 g of solvent is needed for the calculation, it is necessary to drain the contents of the pipette into a weighing bottle and weigh to 0.01 g. This determination of the weight of the pipetted sample should be made once for each solution. Two samples are withdrawn for titration with $0.1N$ sodium hydroxide, and if they do not agree, additional ones are taken to give the average of a larger number.

The solution is diluted with chilled distilled water to give a concentration about half as great, and the resulting constant temperature and concentration are determined.

The bottle is emptied and rinsed and filled about one-quarter full with approximately $0.25N$ acetic acid (about 15 ml of glacial acetic acid in 1,000 ml of water) which has been cooled nearly to zero. An equal volume of finely divided pure ice is added after first rinsing by decantation with cold distilled water. A second set of measurements is made with the solution diluted to about half its concentration with water.

The determinations are repeated with $0.25N$ monochloroacetic acid.

Calculations.—The molecular weights of each of the three solutes are calculated at two different concentrations, using formula (1). The freezing-point depression ΔT_f is the difference between the temperature of freezing water and the freezing solution.

The value of the molal freezing-point depression K_f is given for various solvents in the following table:

MOLAL FREEZING-POINT CONSTANTS

Solvent	Freezing point (t_f)	Molal depression (K_f)
Water	0.0	1.855
Acetic acid	17.	3.9
Benzene	5.4	5.12
Bromine	− 7.3	9.7
Naphthalene	80.0	6.8
Nitrobenzene	5.3	7.0
Phenol	38.5	7.4

The molal freezing-point depression may be calculated from the heat of fusion l_f per gram, the freezing point T_f,* and the gas constant R, by

* As is customary, T represents absolute temperature and t designates centigrade temperature.

the following equation (van't Hoff):

The acetic acid is a weak electrolyte which is dissociated to such a slight extent that it can barely be detected.   In water solution it is not associated into double molecules.

The hydrochloric acid is a strong acid which is completely dissociated, and the depression of the freezing point would be twice that of an undissociated acid except for the interionic attraction.   Accordingly the depression will be somewhat less than twice, the molecular weight will be somewhat more than half, and the interionic effect will be greater in the more concentrated solutions. Since the hydrochloric acid is a strong electrolyte, it is meaningless to apply equation (2) in this case.

The monochloracetic acid is an example of a weak electrolyte that is partly dissociated. The extent of the dissociation is calculated at the two concentrations with the help of formula (2).

Alternative Beckmann Method.—In the Beckmann method shown in Fig. 21 a test tube with a side arm is fitted with a cork that holds a 0.01° thermometer and a ring stirrer made from a small glass rod.   The stirrer moves up and down through a piece of tubing inserted in the cork, and the ring is of such dimensions that it cannot hit the thermometer bulb.   The side arm is for the purpose of admitting the solvent and solute.

The tube is surrounded by an air jacket to minimize the cooling rate, and for this purpose the tube is set into a larger test tube provided with a cork ring.   The tube and jacket are inserted in a cover and set into a freezing mixture in a large jar.   The temperature of the mixture should be about 3° below the expected freezing point.
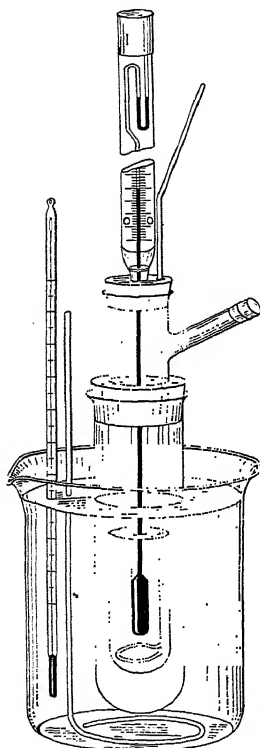
Fig. 21.—Beckmann apparatus for the determination of freezing points.

Then 20.0 ml of distilled water, or a quantity accurately measured to 0.1 ml or less, sufficient to cover fully the thermometer bulb, is introduced from a pipette in such a manner that none of the liquid adheres to the sides of the tube.

The water is cooled quickly until it starts to freeze, and then it is warmed slightly and set into the jacket in the freezing mixture. The stirrer is operated vigorously. The stationary temperature at which the solid and liquid phases are in equilibrium is recorded as the freezing point of the solvent. The thermometer must be tapped *gently* before a reading is taken. The system is warmed, and the freezing point is again determined, the operation being repeated two or three times. If supercooling occurs, the ice will not come out until the temperature is below the correct freezing point; then the temperature will rise, as heat is evolved by the solidification. The temperature will rise to a steady stationary temperature if the solvent is pure. The super-cooling may be relieved by vigorous stirring, but in extreme cases it may be necessary to add a very small crystal as a nucleus for crystallization.

A sufficient quantity of solute to give a depression of about 0.5° is pressed out in a tablet machine and weighed accurately. It is introduced into the apparatus through the side arm, and the freezing point is determined as described for pure water. Supercooling must be minimized. A second determination may be made after adding another weighed amount of solute.

For the solute, urea or sugar may be used as a nonelectrolyte and sodium chloride or potassium chloride as an electrolyte.

This method uses smaller quantities of material and is suitable for benzene and other nonaqueous solutions. It can be used for any weighable solute and is not limited to solutions that can be readily analyzed. Liquids may also be used as solutes.

The molecular weight of an "unknown" is determined.

Practical Applications.—The freezing-point method is the simplest and perhaps the most accurate method for determining molecular weights in solution. It is useful in establishing the formulas of organic substances.

The freezing-point method constitutes one of the best ways for obtaining the activities of solute and solvent for thermodynamical calculations.

Theories of solution can be studied advantageously with these measurements.

Suggestions for Further Work.—Several different ionizing and non-ionizing solutes may be investigated in water and in benzene and other solvents.

According to the best technique,[1,2,3] twin flasks are used, one for the pure solvent and one for the solution, and the temperature difference is determined with a sensitive thermocouple. The thermocouple described on page 425 may be used, and calibrated with the hydrochloric acid solutions in a test tube, vigorously stirred, and cooled with salt and ice until the first ice appears and a steady deflection is obtained. Exactly $0.25N$ hydrochloric acid has a freezing point of $-0.890°$.

The molal freezing-point depression may be determined in concentrated solutions at different concentrations.[4]   In dilute solutions and with nonhydrated salts it does not change much, but in concentrated solutions of hydrated salts (*e.g.*, calcium chloride) it increases considerably.   This fact is of theoretical interest.

An excellent solvent for freezing-point determinations is heptachloropropane, which melts at 29.5° and has a large freezing-point constant.[5]   Another valuable solvent, giving a molar depression of several degrees, is fluoropentachloroethane.[6]

Conditions for obtaining an ice bath constant to 0.001° are described by White.[7] The ice in a covered beaker is protected against melting with a second ice bath, and pure, chilled water is passed through the inner bath at intervals to remove solutes from the surface of the ice.

The solutions may be analyzed conveniently with an immersion refractometer.

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17. Distillation of Binary Mixtures

The composition-temperature curves are determined for both the vapor and the liquid phases.   Electrical heating is used, and the analyses are made with a refractometer.

Theory.—When two liquids are dissolved in each other, the composition of the vapor will differ from that of the liquid if the vapor pressures of the two components are different.

In an ideal solution each component exerts a partial pressure p which is equal to the vapor pressure p_0 of the pure component multiplied by its mole fraction N in the solution.   Expressed in symbols

$$p = Np_0 \tag{1}$$

If the solution is ideal, the molecules of one component are unchanged by surrounding them with the molecules of the other component.

In most solutions, however, there is some type of interaction of one component on the other so that equation (1) does not hold.   There may be a tendency for chemical action, forming a compound in solution as, for example, in a chloroform and acetone mixture.   In other cases one component becomes less volatile in the presence of the other owing to the formation of nonvolatile ions.   In still other solutions the

presence of the second liquid breaks down the larger units of the first liquid and renders the first liquid more volatile.

If a liquid has a low vapor pressure, it must have a high boiling temperature, and, in general, the boiling point–composition curves are just opposite in character to the vapor pressure–composition curves.

In an ideal solution the vapor and liquid composition curves run smoothly between the two boiling points, but in a nonideal solution, particularly if the boiling points are fairly close together, the increased or decreased volatility due to the chemical influence of the other component may be sufficient to cause a minimum or a maximum in the boiling-point curve (corresponding to a maximum or a minimum in the vapor-pressure curve).

As an example of an ideal solution a mixture of methanol and ethanol may be taken.

Hydrochloric acid and water offer a good illustration of a pair that has a maximum boiling point.

A mixture of benzene and methanol is taken as an example of a pair of liquids exhibiting a minimum in the boiling point–composition curve, or a maximum in the vapor-pressure curve.

Apparatus.—A 50-ml distilling flask, modified as shown; short condenser; pipette of about 1 ml; resistance wire for electric heater; step-down transformer; (110 volt to 6 volt); 0.1° thermometer; refractometer; weighing bottle; benzene; methanol.

Procedure.—The apparatus shown in Fig. 22 may be readily constructed from a 50-ml distilling flask. Superheating is avoided by internal electric heating with a resistance coil and a small step-down transformer of at least 25 watts or a 6-volt storage battery.

The heating coil of No. 26 nichrome wire about 14 cm long is wound in the form of a helix, about 2 cm in diameter. It is soldered to lead wires of No. 14 copper wire set into the cork and arranged so that the thermometer bulb is surrounded by the helix. The coil should touch the bottom.

Other types and sizes of resistance wire may be used, but the current should be such that the wire is heated to a dull red heat when out in the open air. A heater of 2 ohms operating at 6 volts is satisfactory.

A 0.1° thermometer reading from 50 to 100° serves very well, but an accurate 1° thermometer with large divisions will do. Its bulb is completely immersed in the liquid, but it must not touch the heating wire.

The arm of the distilling flask is bent upward to act as a reflux condenser; at the bottom of the bend is a bulb of about 1 ml capacity

to act as a pocket for retaining condensed distillate as it flows down from the short condenser.

The transformer is adjusted so that the liquid boils vigorously at a constant rate, and the vapor condenses in the reflux condenser.   Additional regulation may be accomplished with a rheostat, if necessary.
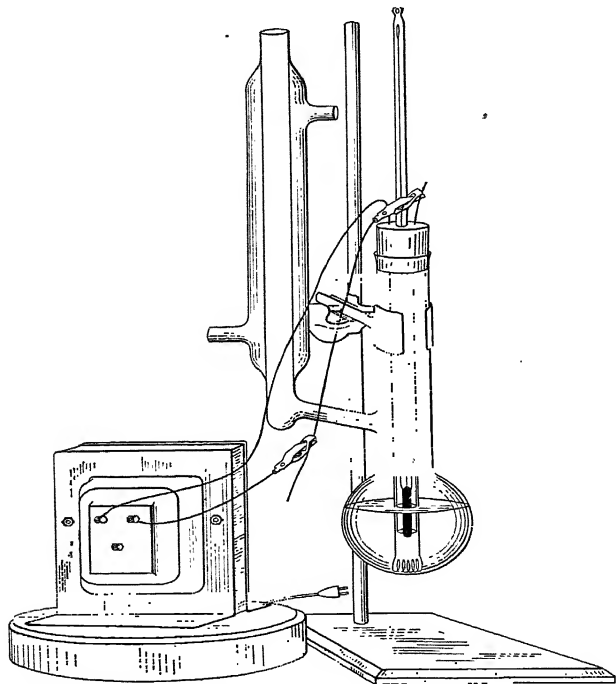
FIG. 22.—Flask for determining the vapor composition of binary mixtures.

The boiling is continued, until the pocket below the reflux condenser has been thoroughly rinsed out with condensed liquid and the thermometer has become constant.   The current is then turned off, the cork containing the thermometer and heating coil is removed, and small samples of about 1 ml are taken with a small tube or pipette from the distillate in the pocket and then from the residue in the flask. The pipette should be dry when taking the samples.   The samples are easily analyzed with an Abbe refractometer.   If it is more convenient

to analyze a whole series of samples at one time, these may be preserved in small *stoppered* vials or test tubes. The sample of distillate is removed by inserting the end of the pipette through the open end of the reflux condenser directly into the pocket below.

About 25 ml of benzene is placed in the flask, and its boiling point is determined. Another determination is made after adding 0.2 ml of methanol, 0.5 ml more, and again after adding 1 ml more. Further determinations are made after three successive additions of methanol, approximately 5 ml being added each time.

The boiling flask is drained and dried, and about 25 ml of methanol is added for a boiling-point determination. Boiling points and compositions of the residue and distillate are then determined after successive additions of benzene as follows: approximately 2, 4, 5, 7, and 10 ml.

The barometer should be read occasionally. In case the atmospheric pressure changes considerably, it is necessary to estimate a correction for the boiling point, taking an average correction for the two liquids as an approximation.

It is necessary to determine the refractive index of the benzene, the methanol, and the mixtures in which each liquid is accurately weighed out in a weighing bottle. Mixtures about 5 ml in volume containing approximately 1 volume of methanol to 1, 3, and 6 volumes of benzene are convenient.

Calculations.—The refractive indices of the weighed samples and the pure liquids are plotted against the compositions of the mixtures expressed in mole fractions (defined on page 454). The composition in mole fractions of each sample of distillate and residue may then be determined by interpolation on the graph.

In a second graph two curves are plotted: one in which boiling temperature is plotted against the mole fraction of the residue, and one in which the same boiling temperatures are plotted against the mole fractions of the distillate. The mole fractions are plotted along the horizontal axis.

The significance of this graph is to be discussed and the composition of the distillate and residue specified after continued distillation under a variety of conditions.

Practical Applications.—Vapor-composition curves are necessary for the intelligent separation of liquids by distillation. Fractional distillation under controlled conditions is essential in the purification of liquids and in many industries such as the petroleum industry and the alcohol and solvent industries.

In addition to plotting the temperature-composition curves it is instructive to calculate the partial pressures.

Suggestions for Further Work.—Other binary mixtures may be studied.

A mixture of chloroform and acetone, giving a maximum in the boiling-point curve, may be studied in exactly the same manner described for methanol and benzene.

The maximum in the boiling-point curve of hydrochloric acid and water falls at 108.5° and a composition of 20.2 per cent hydrochloric acid. The experiment may be carried out in an ordinary 500-ml distilling flask, taking samples of distillate and residue with a 5-ml pipette and titrating with $0.1N$ sodium hydroxide. The temperature is recorded at the time the samples are taken. The thermometer is placed inside a 1-cm glass tube in which a couple of holes are blown. The bottom of the tube and the thermometer bulb which is flush with it are kept a few millimeters above the surface of the liquid. When the liquid boils, it rushes up in the tube and circulates around the thermometer bulb. Superheating is not likely in a region where the liquid is dispersed with small bubbles of vapor. Solutions of different composition are placed in the flask—from half-normal to concentrated. The composition of the liquid phase is conveniently changed by distilling part of the liquid away.

The distillate at the maximum boiling point is so reproducible in composition at a given pressure and so easily obtained that it is a very satisfactory standard solution for volumetric analysis. A solution of hydrochloric acid is made up roughly to approximate the constant boiling mixture, and after discarding the first third the remaining distillate is retained. The barometer is accurately read, and the corresponding composition is obtained from the literature.[9]

Chloroform and methanol, giving a minimum in the boiling-point curve, may be studied by using a Westphal density balance for determining the compositions instead of a refractometer. A density–mole fraction curve is plotted, and the composition of the samples is determined by interpolation. Since larger samples are needed for the density measurements, more material and a larger flask are required.

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18. Fractional Distillation

In this experiment the efficiency of a fractionating column is determined, and the separation of two liquids boiling within a narrow temperature range is studied.

Theory.——The separation of liquids by distillation is one of the oldest and most important operations of chemistry, but considerable improvement has been made in recent years in the design of apparatus for fractional distillation. The developments in petroleum refining and the need for increased efficiency in laboratory operations and purification have been largely responsible for these improvements. More recently the concentration of isotopes has made still greater demands on fractional distillation.

The theory of fractional distillation has been well treated by McCabe and Thiele[3] and is discussed in textbooks on chemical engineering.[4] Successful separation of liquids depends on several factors such as the height of the column, the type of packing, the amount of liquid retained in the column, the insulation, and the reflux ratio.

Since the height of the distilling column is usually limited by the height of the ceiling and the quantity of liquid held up in the column, it is necessary to fill the tower with material that will give a large surface and still leave a large free volume and as small a holdup of liquid as possible. Several efficient types of packing are now available as described on page 338.

To avoid complications due to condensation of the vapor along the walls of the column, it is customary in quantitative-distillation studies to use either a vacuum jacket, a jacket of effective insulating material, or a jacket that can be maintained at the proper temperature either by electrical heating or by the circulation of hot or cold liquids.

The study of the efficiency of different distilling columns has been put on a quantitative basis by the invention of the term *theoretical plate* which is defined as a layer of liquid or section of a distilling column of such length that the vapor just comes to equilibrium with the liquid, in this region. This theoretical plate may be visualized as a layer of liquid in a cap through which the vapor bubbles, as a long length of tubing with a liquid film along the inside wall, or as a short section of efficient packing holding condensed liquid on its surfaces. An ordinary 1-cm tube 1 m long might be equivalent to only one theoretical plate, whereas the same tube filled with adequate packing can give the equivalent of 20 or more theoretical plates. A column with 12 theoretical plates is adequate for the practical separation of benzene and toluene. The number of theoretical plates required for a given separation increases when the reflux ratio is decreased, *i.e.*, when the amount of condensed vapor returned to the column is decreased and the amount distilled off becomes greater. It increases also when materials of higher molecular weight are used.

The number of theoretical plates cannot be determined from the geometry of the distilling column; it is calculated from the separation effected with a liquid mixture, the vapor and liquid compositions of which are fully known.

Apparatus.—Fractionating columns, packing for fractionating column; electrically heated jacket; adjustable resistance or reactance to control temperature of heating jacket; distilling flask to fit fractionating column; oil bath with heating coil; rheostat for controlling temperature of oil bath; still head with two condensers, one for distilling and one for refluxing, one of which is adjustable for varying reflux ratios; three 1° thermometers; 100-ml graduated cylinders; Abbé refractometer; carbon tetrachloride, benzene.

Procedure.—A distilling apparatus is set up as shown in Fig. 23. It is arranged with standard ground-glass joints so that different fractionating columns may be used with the same still head, jacket, and distillation pot. Rubber stoppers can be substituted if inert liquids are used. A suitable heating jacket for the column may be made by placing around the central tube a 6-cm pyrex tube with asbestos board or "transite" plates at each end held together with tie rods. Eleven meters of resistance wire in the form of four long spiral coils of No. 22 nichrome wire run the length of the jacket, and the air is heated by adjusting the electrical current with a reactance or rheostat so as to keep the jacket temperature registered on the outer thermometer about 5° below that of the central thermometer. In the Henke arrangement the coils are packed closer together at the bottom to equalize the temperature. Asbestos covering around the distilling column may be substituted for the electrically heated air jacket.

The fractionating column of pyrex is about 16 mm in diameter and 70 cm high. Ground-glass joints are fused to the ends. One column is empty, and the other is filled with a standard packing such as the Stedman double cones of stainless-steel gauze (page 339).

The efficiencies of the simple tube and one or more packed columns are to be determined by calculating the number of theoretical plates. For this purpose the extent of separation of a mixture of benzene and carbon tetrachloride is measured.

The distilling pot has a capacity of about 250 ml and is heated in an oil bath containing an electric heating coil (5 m of No. 24 nichrome wire) connected to the 110-volt circuit through a rheostat. The temperature is adjusted to give vigorous but not violent boiling. The pot has a side arm through which small samples of the liquid may be removed for analysis with a tube or pipette. The still head is provided with an exit and water condenser and an adjustable condenser. When the water-cooled tube is pushed far into the

rubber collar, all the condensed liquid drips off the tip and falls back onto the packing in the fractionating column. By pulling the condenser out to different positions the amount of condensate returned to the column and that allowed to drain out may be varied at will. The number of drops of liquid per minute distilling into the collector
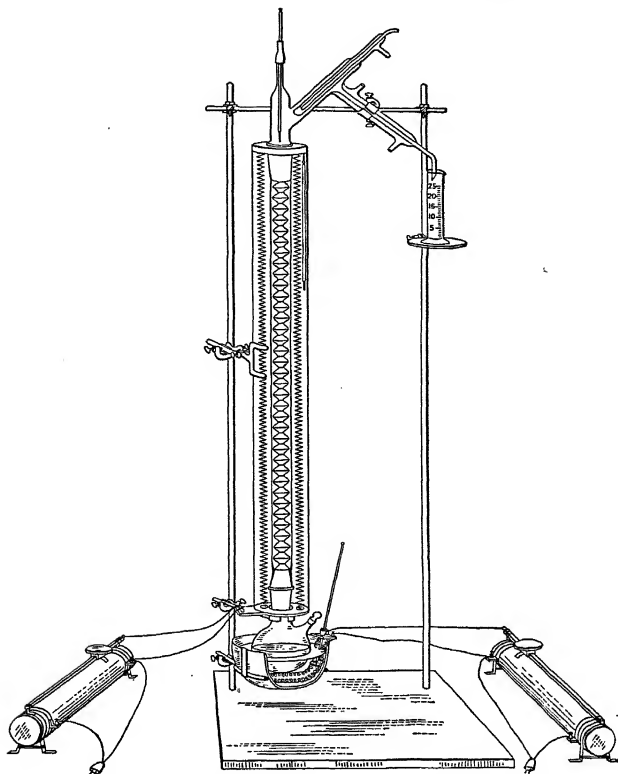
Fig. 23.—Apparatus for fractional distillation.

and the number returning to the distillation pot are counted. The reflux ratio is defined as the ratio of the amount of liquid returned to the fractionating column to the amount distilled out.

About 20 ml of carbon tetrachloride and 30 ml of benzene are mixed and placed in the distillation pot. A few drops are removed for

immediate analysis with an Abbe refractometer, or they are stored in a small stoppered bottle for later analysis. A plain unpacked tube is placed between the boiling liquid and the still head. The oil bath is heated to a steady temperature at which vigorous boiling occurs, and the reflux condenser is arranged so that a steady stream of condensed vapor drops from the condenser back to the vapor column and none is distilled out. The heating current in the jacket is adjusted so that the thermometer registers about 5° below the central thermometer. After equilibrium is attained and the central thermometer remains constant for several minutes, the condenser is pulled out to such a position that the number of drops of liquid returned per minute to the distillation pot is about twice the number distilling out giving a reflux ratio of 2 to 1.

The first two or three drops are discarded, and then a 1-ml sample is collected for analysis with the refractometer. The heating bath is lowered temporarily while a sample of the liquid (about 1 ml) is removed from the distillation pot, using a pipette or tube with a finger placed over the top.

Then a fractionating column with Stedman packing or other packing is fitted to the distillation pot, and the procedure, just described, is repeated. With the packed column it is necessary to boil the solution for half an hour to an hour with a steady stream of liquid returning from the condenser before the thermometer reaches a steady reading. Then the condenser is pulled out as before to give a 2 to 1 reflux ratio and two samples are taken from the distillate, after discarding the first few drops, and two more from the distillation pot. From these data the number of theoretical plates in the fractionating column is calculated.

While equilibrium is being established in the fractionating column, refractive-index measurements are made on the pure benzene, pure carbon tetrachloride, the original mixture, and perhaps one or two other mixtures of known composition. A drop or two of the liquid is placed in the Abbe refractometer (page 47). These measurements are used for determining the composition of samples of distillate and residue.

After determining the number of theoretical plates the packed column is used next to determine the separation of two liquids. The column and distilling pot are emptied and dried and 15 ml of carbon tetrachloride and 15 ml of toluene are introduced. With the reflux condenser set for a reflux ratio of about 2 to 1 the liquid is boiled out and collected in a graduated cylinder. A 1-ml sample is collected in a small stoppered tube after every 3-ml of distillate. The refractive indices are then recorded together with the total volume distilled over.

Calculations.—The refractive indices of the benzene, the carbon tetrachloride, and one or two known mixtures of the two are marked on coordinate paper on which the mole per cent of carbon tetrachloride is plotted along the X-axis from 0 to 100. A nearly straight line is drawn through these points. It cannot be assumed that all binary mixtures will give straight lines when refractive index is plotted against mole per cent.
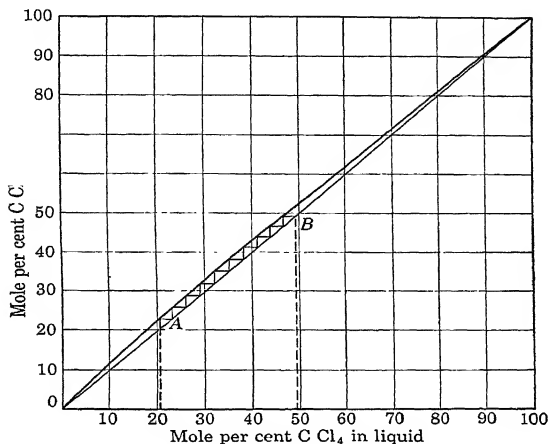
FIG. 24.—Vapor-liquid composition curve.

The number of theoretical plates is calculated with the help of a large graph in which the vapor composition is plotted against the liquid composition as indicated on a small scale in Fig. 24. The data for this graph[5,6] are given in the following table.

LIQUID AND VAPOR COMPOSITION OF MIXTURES OF CARBON TETRACHLORIDE AND BENZENE AT 760 MM AND AT TEMPERATURES BETWEEN THE BOILING POINTS

Mole per cent CCl$_4$ in liquid...............	13.64	21.57	25.73	29.44	36.34	40.57	52.69	62.02	72.?
Mole per cent CCl$_4$ in vapor.	15.82	24.15	28.80	32.15	39.15	43.50	54.80	63.80	73.3

The composition A of the residue in the distillation pot and the corresponding distillate B after refluxing are marked on the line, and a series of vertical and horizontal lines is drawn stepwise from A as

shown until the composition of the distillate is reached. The number of these vertical line steps minus one is equal to the number of theoretical plates in the fractionating column. The liquid-vapor surface in the distillation pot acts as one theoretical plate.

The effectiveness of a column depends on the height as well as the packing. Consequently the efficiency is usually given in terms of the height equivalent per theoretical plate H.E.T.P., obtained by dividing the height by the number of theoretical plates. It is best given in centimeters (sometimes in inches).

The value of the H.E.T.P. is calculated for the single tube and for the packed column.

The effectiveness of distillation is illustrated by plotting the refractive index of the samples collected during distillation against the percentage of the total volume of the mixture distilled. The shape of this curve indicates the efficiency with which the liquids are separated.

Suggestions for Further Work.—The distillation and analysis with the packed column is carried out with a 10 to 1 reflux ratio instead of the 1 to 1 ratio. The greater reflux ratio gives a sharper separation but requires a longer time.

Other packings are used, each in a column that can be readily fitted into the distilling pot and still head.

An impure liquid such as a low-grade technical benzene is purified by fractionating with a 10 to 1 reflux ratio, and the purification is followed by refractive-index measurements on the distillate. Liquids for use in the laboratory may be advantageously purified in this way.

A commercial gasoline may be separated into fractions of different boiling-point ranges.

The value of a fractionating column depends not only on the number of theoretical plates but also on the amount of liquid held up by the packing. The smaller the holdup, the better the column, particularly if the supply of material is limited, and the quicker are equilibrium conditions reached. The amount of liquid held up may be determined at the end of an experiment by removing the heating bath, taking out the column and blowing dry air through it, and condensing the material in a weighed U tube surrounded by a freezing bath of dry ice. When the packing is completely dry, the increase in weight of the U tube gives the weight of the liquid held up in the column.

Additional pairs of liquids may be separated by fractionation with an efficient column. A mixture of carbon tetrachloride and toluene may be used to determine the number of theoretical plates. The data for this system are given in the following table.

LIQUID AND VAPOR COMPOSITIONS OF MIXTURES OF CARBON TETRACHLORIDE AND TOLUENE[5]

Mole per cent CCl_4 in liquid.	5.75	16.25	28.85	42.60	56.05	64.25	78.20	94.55
Mole per cent CCl_4 in vapor.	12.65	31.05	49.35	64.25	75.50	81.22	89.95	97.35

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19. Partial Miscibility

Theory.—Liquids are often miscible in all proportions, but there are a number of pairs in which the solubility of each in the other is limited. Usually, both liquids become more soluble as the temperature is increased, and eventually a critical solution temperature or consolute temperature is reached above which the liquids are miscible in all proportions. In some cases the liquids become more soluble as the temperature is decreased, and in this case there is a critical solution temperature *below* which the liquids are miscible in all proportions.

The temperature-composition curve permits a complete understanding of the behavior of any system of the two liquids, and the interpretation of the curve constitutes an important exercise in the application of the phase rule.

Phenol and water make a particularly suitable pair because the materials are cheap and the critical temperature comes at a convenient temperature, below the boiling point of either component. In cases where the critical solution temperature is above the boiling point of one of the components, the work is done in a closed system.

Apparatus.—An 8-in. test tube; 10-in. test tube with cork; 0.1° thermometer; glass stirrer of the ring type; 2-ml pipette.

Procedure.—A test tube is fitted with a cork, a 0.1° thermometer, and a glass stirrer. The stirrer is made from a small glass rod, bent into a ring of such size that it cannot hit the thermometer bulb. It is moved up and down vigorously by hand. The test tube is enclosed in a larger test tube, fitted with a cork to hold the smaller tube in position as shown in Fig. 25. In this way, an air jacket is provided

to reduce the rate of cooling or heating. The whole apparatus is clamped in position in a large beaker of water which can be heated.

Ten grams of phenol weighed out to 0.1 g and 10 ml of water are placed in the apparatus, and the temperature is raised to about 60°

by setting in boiling water and stirring vigorously. At a certain temperature the mixture suddenly becomes clear because the water and p h e n o l are completely soluble. The tubes are lifted out of the hot water, and the solution is allowed to cool while being s t i r r e d. The solution becomes milky again, and the temperature at which the first turbidity appears should be the same as the temperature noted before at which the solution becomes clear. The opacity is due to the fact that the refractive indices of the two solutions are different. Two or three check determinations are made, with a rising and a falling temperature. Closer agreement is obtained when the temperature is changed slowly.

Two milliliters of water is added from a pipette, and the determination is repeated. This time, the temperature of complete miscibility is higher.

The determinations are repeated, each time adding 2 ml more of water. The temperature of complete miscibility rises, passes through a m a x i m u m, and then decreases. The experiment is continued until the temperature of complete miscibility has fallen to 60°, or below.

FIG. 25.—The determination of the temperature of miscibility in a pair of liquids.

Calculations.—The p e r c e n t a g e composition of the different mixtures is calculated, and the temperature of complete miscibility is plotted against the percentage composition. A correction is made for the exposed stem of the thermometer (page 421). The critical solution temperature is determined from the graph. Every part of the diagram is discussed fully with reference to the phases present, the influence of temperature, and the influence of composition. Special emphasis is placed on the interpretation of a point that lies inside the

curve, and it is to be shown how one may pass from a solution rich in phenol to a solution rich in water without the appearance of two phases.

Practical Applications.—A clear understanding of diagrams of this type is necessary in predicting the properties of many systems and in separating one component from another.

Suggestions for Further Work.—The viscosity of some of the phenol-water mixtures may be determined at different temperatures. When the two phases appear, the viscosity increases greatly, and this phenomenon is important in the theory of emulsions and gels.

It is interesting to determine the effect of a third substance on the critical solution temperature, as, for example, sodium chloride, which dissolves only in the water; benzene, which dissolves only in the phenol; and ethanol, which dissolves in both.

Trimethylamine and water[3] and also methanol and carbon disulfide[4] give a critical temperature similar to phenol and water. Methyl-ethyl ketone and water is a system that has both an upper and a lower consolute temperature. Nicotine and water furnish another example.

Successive small amounts of water are added to ethanol, and an equal volume (*i.e.*, equal to the sum of the two) of kerosene is added. The temperature at which turbidity is produced is plotted against the percentage of water in the alcohol, and the graph is used to determine water in an unknown sample of concentrated alcohol.

The effect of various amounts of different salts on the solubility of phenol in water is interesting.

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20. Steam Distillation

Steam distillation is used to illustrate physical-chemical relationships and to calculate molecular weights.

Theory.—When two immiscible liquids are heated, each exerts its own vapor pressure irrespective of the other. When the sum of the vapor pressures of the two liquids becomes equal to the atmospheric pressure, the two distill over together and the temperature of distillation and the composition of the liquid remain constant until one of the liquids is entirely evaporated.

The composition of the distillate is fixed by the vapor pressures and the molecular weights. The higher the vapor pressure of a liquid, the greater is the number of molecules in the vapor phase; and the larger the molecular weight, the greater is the weight of material evaporated, by a given number of molecules.

Steam distillation is similar to vacuum distillation, in that the liquid distills over and condenses at a temperature much below its normal boiling point.

Apparatus.—A 500-ml distilling flask; condenser; two 100-ml volumetric flasks; 0.1° thermometer; steam generator; glass tubing.

Procedure.—A 500-ml distilling flask is connected to a condenser, and steam is introduced from a generator, made of a metal can pro-
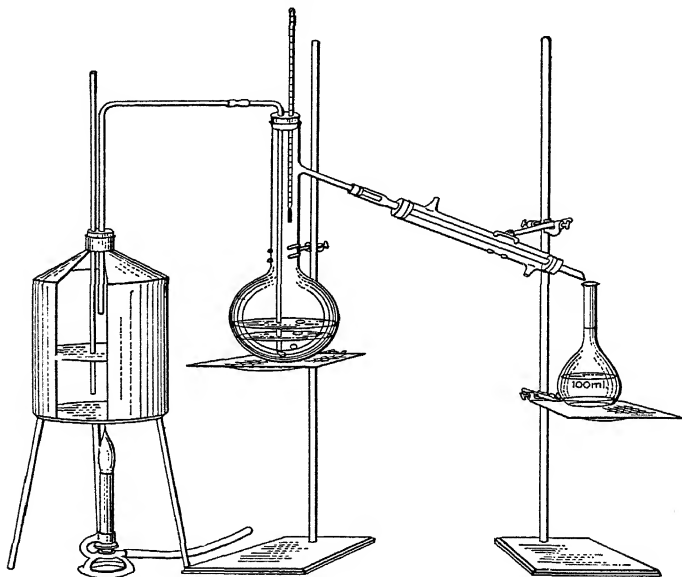
Fig. 26.—Apparatus for steam distillation.

vided with a two-hole stopper carrying the exit tube and a 50-cm safety tube, which extends to the bottom of the can.   If too great a pressure is built up, it is relieved by forcing out the liquid in the safety tube.   The apparatus is shown in Fig. 26.

The enlarged end of the steam-inlet tube at the bottom of the flask has a number of small holes so that the steam will have an opportunity to become saturated with the vapor of the other liquid.   To accomplish this, a thin bulb is blown on the end of a glass tube and perforated with many small holes, using the sharpened end of a file which has been heated to redness.

Live steam is passed through the flask to correct for the exposed stem and errors in the thermometer. The true temperature of the steam is determined by reading the thermometer (corrected to 0° as given on page 421) and finding in tables the boiling point of water at this pressure. The difference between this temperature and the thermometer reading gives the correction which must be added or subtracted. This correction is applicable only when the thermometer is in the same position and the temperature is approximately the same.

About 100 ml of nitrobenzene is introduced into the flask, and steam is forced through the heavy nitrobenzene layer. When the temperature becomes constant, two 100-ml volumetric flasks are allowed to fill to the mark with the distillate and are set aside to allow the layers to separate.

If the distillation is too rapid, an insufficient quantity of nitrobenzene will distill over. Most of the water layer is poured from the collected samples, and the volume of the nitrobenzene layer is carefully measured after transferring it to a small cylinder graduated to 0.1 or 0.2 ml. All the nitrobenzene including small drops clinging to the sides of the flask must be rinsed out into the cylinder.

The meniscus of the nitrobenzene is inverted when covered with water, and an error is introduced if the reading is taken in the usual manner, because the cylinder is calibrated for a meniscus that is convex to the bottom. Two or three millileters of nitrobenzene is placed in the cylinder and covered with a little water. The difference between the level of *this* meniscus and the level *after* pouring in the nitrobenzene from the flask gives the correct volume of nitrobenzene carried over by the steam.

Calculations.—The weight of each component in the distillate is proportional to the vapor pressure and to the molecular weight, as shown by the following relation:

$$\frac{\text{Weight}_A}{\text{Weight}_B} = \frac{\text{vapor pressure}_A \times \text{molecular weight}_A}{\text{vapor pressure}_B \times \text{molecular weight}_B}$$

The experimental data may be used to calculate a number of different quantities. In this experiment, the molecular weight of nitrobenzene is calculated. The weight of nitrobenzene is determined from the volume of the condensed liquid, its density being 1.204 at 20° and 1.197 at 25°. The vapor pressures of water and nitrobenzene at the temperature of distillation are found from tables by interpolation.

Since the liquids are not absolutely immiscible at the temperature of distillation, the two vapor pressures do not add up to give exactly atmospheric pressure, and a slight error is introduced in the calculation.

Practical Applications.—When a liquid decomposes at its normal boiling point, it can be distilled only under reduced pressures, by vacuum distillation or by distillation with steam or other immiscible liquid. The apparatus for steam distillation is simpler than that required for vacuum distillation, but the process is limited to those liquids which are immiscible with water. Water is the most common liquid used in the distillation of immiscible liquids on account of its cheapness and its low molecular weight.

Many organic liquids are purified by steam distillation, particularly those which decompose at their normal boiling points. Sometimes inflammable liquids are distilled with steam to avoid the fire hazard involved in ordinary distillation.

Suggestions for Further Work.—Other liquids may be used instead of nitrobenzene, such as mercury, aniline, fats, and oils.

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21. Partial Molal Properties of Solutions

The accurate determination of the density of a liquid and the precise mathematical treatment of solutions are illustrated.

Theory.—The quantitative study of solutions has been greatly advanced by the conception of partial molal quantities. A property of a solution, *e.g.*, the volume of a mixture of alcohol and water, changes continuously as the composition is changed, and considerable confusion existed formerly in expressing these properties as a function of composition. G. N. Lewis[1] emphasized the obviously exact and simple methods of differential calculus and defined the partial molal property of a component of the solution as the rate of change of the property of the solution with the concentration. Expressed mathematically, the partial molal volume $\bar{V}$ is the partial derivative of the volume V of the solution with respect to the concentration n of one component, all other components remaining constant. The partial molal volume of one component (water) is given by the expression

$$\bar{V}_1 = \frac{\partial V}{\partial n_1} \tag{1}$$

and the partial molal volume of a second component (alcohol) is

$$\bar{V}_2 = \frac{\partial V}{\partial n_2} \tag{2}$$

The partial molal quantities are designated by a bar above the letter. Heat capacity, heat of solution, or any other property which is of an additive nature can be used as well as volume. The volume V of the solution is equal to the sum of the volumes of all the components

in the solution; and the volume of a component is equal to the number of moles n of that component multiplied by its partial molal volume. Mathematically expressed,

$$V = n_1\bar{V}_1 + n_2\bar{V}_2 + n_3\bar{V}_3 + \cdots \tag{3}$$

In the case of ideal solutions, the volume of a component in solution is identical with the volume of the same component in the pure state. For example, if ethanol and water formed an ideal solution, the molal volume of a solution containing half a mole fraction of each would be given by the expression

$$V_{n_1=n_2=0.5} = n_1\bar{V}_1 + n_2\bar{V}_2 = 0.5(18) + 0.5(58.6) = 38.3 \text{ ml}$$

Here 18 and 58.6 are the molal volumes of the two liquids. Actually the volume of the solution is 36.9 ml because the alcohol and the water are changed in character by mixing them. New compounds are formed between the two, or there is a change in the equilibrium between different types of associated molecules, such as $(H_2O)_n$. The effect of each of these changes is complicated and difficult to predict, but the total effects are easily measured and readily expressed mathematically, as already shown.

The partial molal volume can be visualized by considering a large reservoir of the solution, so large that the addition of one more mole of water will not appreciably alter the concentration. When 18 ml of water is added to a large excess of water, the volume of the liquid will increase by 18 ml, but when the 18 ml of pure water is added to a solution of mole fraction 0.5, the volume of the solution will increase only 16.8 ml. This increase in volume of the solution per mole of water added under conditions of constant composition is the partial molal volume of water.

There are several methods for determining partial molal volumes from experimental data by graphical means. These methods are described fully by Lewis and Randall.[1]

Apparatus.—Pycnometer; thermostat; balance; six small bottles and stoppers; ethanol.

Procedure.—About 25 ml of solutions of ethanol and water are made, containing approximately 0, 20, 40, 60, 80, and 100 per cent alcohol. The ethanol and water are weighed out accurately into a weighing bottle, care being taken to prevent evaporation. The solutions are transferred quickly to small bottles and kept tightly stoppered.

The density of each solution is determined accurately, at 25.0°C., with a pycnometer of the Ostwald-Sprengel type (shown in Fig. 27).

The pycnometer is dried carefully, weighed, and then filled with freshly boiled and cooled distilled water.   It is suspended in a thermostat for 10 or 15 min., and as the water expands with the rise in temperature, the excess is wiped off with a piece of filter paper.   The liquid must come just to the mark in the capillary, but no farther.

When the water has come to the temperature of the thermostat, the pycnometer is removed, wiped with a lintless cloth, and allowed to stand for a few minutes in the balance case before weighing.   A little more water is added, and the determination is repeated.

The pycnometer is next emptied and rinsed thoroughly with one of the solutions.   The weight of the solution required to fill the pycnometer is determined in the manner just described.
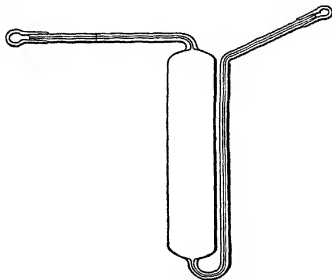
Fig. 27.—Ostwald-Sprengel pycnometer.

The determination is repeated for all the different solutions of ethanol and water.

Two pycnometers may be used to advantage so that one may be weighed while the other is in the thermostat.

Calculations.—The volume of the pycnometer at 25° is calculated from the weight of water that it contains, all weighings being reduced to vacuum.   The density of water at 25° is 0.99707.

The density of the solution is calculated by dividing the weight of the solution by the volume of the pycnometer.   The specific volume, *i.e.*, the volume occupied by 1 g of the solution, is obtained by dividing the volume of the pycnometer by the weight of the solution. The densities may be checked with values found in tables.

The specific volumes of the solutions are plotted accurately on graph paper against the percentages of ethanol, and a smooth curve is drawn through the points.   A tangent to the curve is drawn accurately at one concentration and the intercept on the 0 per cent ordinate gives the partial specific volume of the water at that concentration, and the

intercept on the 100 per cent ordinate gives the partial specific volume of the ethanol. The partial molal volume is obtained by multiplying the partial specific volume by the molecular weight.

Two curves are drawn on coordinate paper, one giving the partial molal volume of ethanol and the other the partial molal volume of water, plotted in each case against the mole fraction. The mole fractions are plotted on the X-axis from 0 to 1. The sum of the two ordinates, each multiplied by its mole fraction, gives the molal volume of the solution at a given concentration.

The data (for the more dilute solutions of ethanol) are plotted also in a different way. The concentrations are expressed in terms of molality rather than in percentage. A molal solution contains 1 mole of solute in 1,000 g of solvent. The volumes of these different solutions (each solution containing 1,000 g of solvent) are plotted carefully against their molalities, and the slope of the tangent at any point gives directly the value of $\delta V/\delta n_2$, where V is the molal volume of the solution and n_2 is the number of moles of solute dissolved in 1,000 g of solvent. The partial molal volumes of ethanol calculated by this method are compared with the values obtained by the preceding method.

Practical Applications.—Properties of solutions of this type can be expressed most accurately in terms of partial molal quantities.

The volume of a solution, at any concentration, can be calculated from the partial molal quantities, and the composition with the help of equation (3).

Suggestions for Further Work.—Other solutions may be investigated, such as methanol and water, benzene and carbon tetrachloride, salt and water.

Data on densities or specific heats of solutions may be taken from tables and calculated in the manner described above.

The partial molal volumes may be calculated by a more accurate method described by Lewis and Randall.[1] In this method, the apparent molal volume is plotted against the logarithm of the number of moles of solute, and a tangent is drawn to the curve. The partial molal volume of the solute at any point is obtained by dividing the slope of the tangent by 2.303 and adding the apparent molal volume. To obtain the apparent molal volume, the volume of the pure solvent present in the solution is subtracted from the volume of the solution, and the difference is divided by the number of moles of solute. This method is more accurate, because the errors of graphing are concerned only with a correction term (the difference between the partial molal volume and the apparent molal volume).

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CHAPTER V

THERMOCHEMISTRY

22. Heat of Combustion

Experience is gained in the operation of a combustion bomb calorimeter and in the calculation of calorimetric data.

Theory.—Among thermochemical reactions, the oxidations are the most common and the most important. Nearly all organic compounds can be oxidized completely, and the reactions proceed rapidly. They are, therefore, suitable for experimental measurement, and the heats of combustion are used extensively in the various calculations of thermochemistry. According to an important theorem of thermodynamics, the free energy and the equilibrium constant of a reaction can be calculated from the heat of reaction and one additional quantity, the entropy change. Heat-of-combustion data are finding extensive use, also, in the field of molecular structure. They give valuable information concerning the nature of the chemical bond and permit estimations of heats of dissociation.

A powerful oxidizing agent is needed to oxidize all the material to the highest state of oxidation, and in accurate work the material is exploded in a heavy steel bomb with oxygen under a pressure of about 25 atm. A special acid-resisting alloy of steel is used in the construction of the bomb, because water and nitric acid are always produced in the explosion, and particularly in the case of organic compounds containing nitrogen there may be considerable acid formed.

The adiabatic method of calorimetry is convenient. It eliminates the cooling correction by keeping an outer bath always at the same temperature as the calorimeter; in this way the accuracy is increased and the calculation simplified. Accuracy is increased because corrections for radiation, evaporation, and thermometer lag are eliminated.

Measurements in a bomb calorimeter are made under conditions of constant volume, and no work is done against the atmosphere. Most other thermochemical measurements are carried out at constant pressure. The heat of reaction at constant pressure may be calculated from the heat at constant volume by adding the work done against the atmosphere. This work is given by the expression $P\Delta V$, where ΔV is the increase in volume and P is the pressure. It is more convenient

to use the equivalent expression $(n_2 - n_1)RT$, where n_2 is the number of moles of gaseous products, n_1 is the number of moles of reacting gases, R is the gas constant (1.987 cal. per degree), and T is the absolute temperature. The volumes of liquids and solids are so small that they may be neglected.

Apparatus.—Parr, Emerson, or other adiabatic calorimeter; pellet machine; two thermometers graduated to 0.01°; iron wire; benzoic acid, naphthalene, sugar; 0.1N sodium hydroxide.
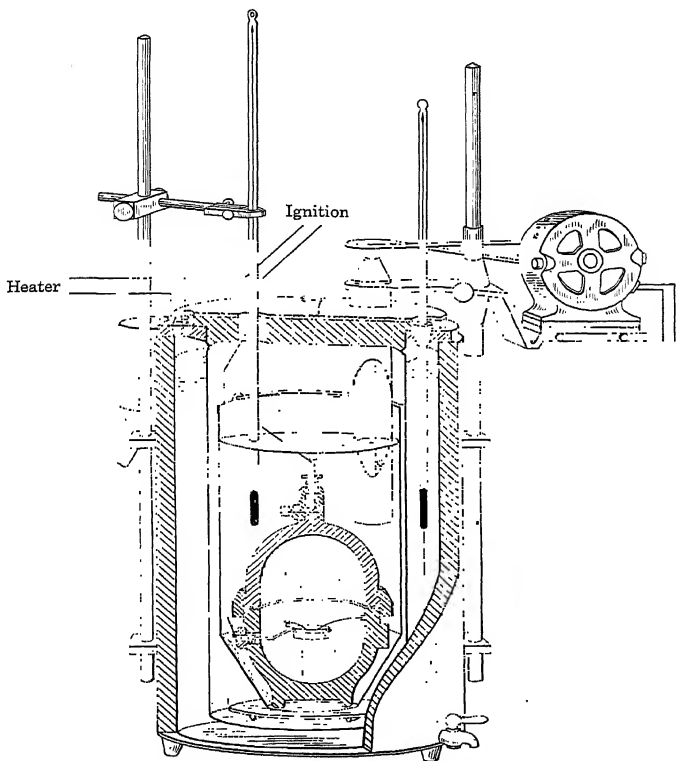
FIG. 28.—Emerson adiabatic combustion calorimeter.

Procedure.—The Emerson calorimeter is shown in Fig. 28. A little less than 1 g of the material to be oxidized is pressed into a pellet

with the pellet machine. A weighed iron wire, about 0.2 mm in diameter, is incorporated in the pellet by setting it into the steel receptacle of the machine before filling. The weight of the pellet is obtained by subtracting the weight of the wire from the weight of the pellet and wire. If possible, the material is pressed into a pellet to prevent the mechanical loss of unburnt materials during the explosion. Coal and some other materials are difficult to make into pellets, and under these conditions the material is simply weighed in the pan and packed around the ignition wire.

The pellet is suspended over the little pan that is attached to the cover of the bomb, the ends of the wire being attached to the two supporting rods in such a way as to complete the electrical circuit. One of the terminals is connected to the lighting circuit through the bomb and calorimeter. The other terminal is insulated from the cover of the bomb and is connected directly with the lighting circuit through a large lamp or other resistance which allows the passage of 3 or 4 amp. when the switch is closed. A double-pole switch is used.

The bomb is set into a steel receptacle on a firm table, and the cover, holding the suspended pellet, is placed in position. The heavy ring is then screwed down, clamping the cover firmly onto the bomb. The final tightening is accomplished with the help of a spanner wrench with a handle 50 or 100 cm long.

The cap, which is connected by a metal tube to an oxygen tank, is then screwed over the valve of the bomb, and oxygen is admitted slowly until the pressure gage reads 25 atm. The valve of the tank is closed, and the pressure in the pipe line is relieved by opening the stopcock so that the cap may be unscrewed. The valve of the bomb prevents the escape of the oxygen.

Approximately 2,000 ml of distilled water is weighed into the calorimeter. The bomb is placed in the water, and the calorimeter is then transferred to the adiabatic jacket. The water must cover the bomb. If gas bubbles escape from the bomb, the cover must be screwed on more tightly, or the large gasket and the washer in the valve may need replacement. If the charge is ignited while a slight leak is present, the bomb may be seriously damaged. The ignition wire is connected to the bomb, and the cover of the calorimeter is set in place.

The thermometers are lowered into position, and the jacket is heated by closing the electrical circuit to make the temperature the same as that in the calorimeter within 0.02 or 0.03°. Alternating current passes directly through the water of the outer jacket.

Thermometers reading from 20 to 30° are preferred, but Beckmann thermometers may be used if care is taken to set them both alike.

For precise work the thermometer in the inner can must be standardized. The temperature must be such that the mercury is on the lower part of the scale, for if the rise in temperature is sufficient to cause the mercury to go above the top of the scale, the determination is lost.

The thermometer is read for a few minutes to make sure that adiabatic conditions have been attained and that there is no further change of temperature. This temperature is recorded as the initial temperature. The ignition switch is closed, and the lamp should glow momentarily and then go out, indicating that the iron wire has burned and fired the charge. The switch is opened at once so that heat will not be introduced by the passage of electricity through the water in the inner calorimeter.

The temperature of the calorimeter rises very quickly, and the jacket thermometer is kept even with the calorimeter thermometer by closing the switch in the heating circuit as needed. The temperature rise becomes slower, and after 4 or 5 min. the temperature again becomes stationary. During the rapid rise of the thermometer, it may not be possible to keep the two thermometers reading exactly alike, but toward the end of the experiment they can be kept within a few hundredths of a degree.

When the final temperature has been reached, as evidenced by the fact that there is no further change, the bomb is removed, the pressure is relieved by pressing in the valve, and the cover is removed. The bomb is rinsed out with a little water, which is then titrated with sodium hydroxide to determine the amount of nitric acid formed from the nitrogen of the air originally present and from the nitrogen contained in the compound, if any. The weight of the unoxidized iron wire is determined.

In the Parr calorimeter the outer jacket is heated by running in hot water through a gas heater. In this type the water circulates through the cover also.

The bomb and calorimeter are thoroughly cleaned and dried and made ready for the next determination.

Two determinations are made with benzoic acid for calculating the heat capacity of the calorimeter and two determinations with a substance whose heat of combustion is accurately known such as naphthalene or sugar. The materials must be highly purified. Then the heat of combustion of a sample of coal or other "unknown" is determined.

Calculations.—The heat capacity of the calorimeter includes the heat absorbed in raising the bomb, thermometer bulb, calorimeter cans, stirrer, and other accessories through 1°. It cannot be cal-

culated accurately from the specific heats of the materials but must be determined experimentally by difference, under actual working conditions.

For every gram of benzoic acid burned, 6,315 cal. of heat is evolved in the calorimeter, and for every gram of iron wire oxidized, 1,600 cal. is introduced. The total heat supplied to the calorimeter is calculated from the weights of benzoic acid and wire and the heat produced by the formation of nitric acid (approximately 15,000 cal. per mole).

The heat absorbed by the water is obtained by multiplying the temperature rise by the heat capacity of the water (approximately $2,000 \times 0.999$). The difference between the total heat evolved and the heat absorbed by the water represents the amount of heat absorbed by the calorimeter. The heat capacity of the calorimeter is obtained by dividing this difference by the temperature rise.

The heat capacity of the calorimeter having been determined, the heat of combustion of naphthalene or any other substance can be calculated.

The heat capacity of the calorimeter is added to the heat capacity of the water, and the sum is multiplied by the temperature rise, to give the total heat evolved. From this heat are subtracted the heats evolved by the combustion of the known weight of iron wire and by the formation of the nitric acid. The heat evolved by 1 g of the material and by 1 mole is calculated.

Practical Applications.—Various heats of reaction and heats of formation can be calculated from the heats of combustion. For example, the heat of oxidation of carbon to carbon monoxide may be obtained by subtracting the heat of combustion of carbon monoxide from the heat of combustion of carbon. In fact, the majority of the thermochemical data have been calculated from heats of combustion.

The heating value of fuels and the calories associated with different foods are determined directly by this method.

Suggestions for Further Work.—The heat of combustion of other pure organic substances may be determined and checked with the accepted values.

The heating value of various samples of coal or food may be determined. These materials cannot be readily made into pellets, and they are placed in the pan around the ignition wire. The oxygen must be admitted slowly to prevent scattering of the powder. With coal, a 0.5-g sample is sufficient.

Liquids may be used if they are sealed off in thin, flat, glass bulbs and weighed. A weighed quantity of benzoic acid or naphthalene is placed on the bulb, and its combustion breaks the glass and permits the combustion of the liquid.

Additional material on heats of combustion is given on page 346.

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23. Heat of Neutralization

This experiment gives practice in a simple calorimetric determination and illustrates the heat effects accompanying certain inorganic reactions.

Theory.—The neutralization of an acid HA and a base BOH may be represented by the ionic equations

$$\mathrm{HA} \rightarrow \mathrm{H^+} + \mathrm{A^-}$$
$$\mathrm{BOH} \rightarrow \mathrm{OH^-} + \mathrm{B^+}$$
$$\underset{\mathrm{H_2O}}{\downarrow} \qquad \underset{\mathrm{BA}}{\updownarrow}$$
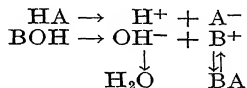
Generally water is the chief product, because the salt BA is largely ionized. If the acid and base are highly ionized to start with, the only chemical reaction is

$$\mathrm{H^+} + \mathrm{OH^-} \longrightarrow \mathrm{H_2O}. \qquad \Delta H_{298.1} = -13{,}800 \text{ cal.}$$

or if the hydrogen ion is assumed to be hydrated

$$\mathrm{H_3O^+} + \mathrm{OH^-} \longrightarrow 2\mathrm{H_2O}.$$

In dilute solutions, this quantity of heat is evolved in many neutralizations irrespective of the nature of the acid or base. In the case of weak acids or bases, or in concentrated solutions, the base and acid undergo ionization during the process of neutralization and the total heat evolved is not 13,800 cal. Combination between solvent and solute or the breaking down of associated molecules are factors that may be included in the heat of the reaction.

Apparatus.—Two vacuum bottles with ring stirrers (page 74); 0.5N NaOH, 0.5N HCl; 0.5N acetic acid; two 100-ml pipettes; Beckmann thermometer or other thermometer or thermocouple for measuring to a few thousandths of a degree at 25°.

Procedure.—Cylindrical vacuum bottles make excellent calorimeters, because they reduce the cooling corrections to a very low value. A vacuum bottle of the pint size is convenient for many experiments. The bottle, of wide mouth, is provided with a cork, an accurate thermometer, and a ring stirrer of glass tubing, preferably of small heat capacity. The arrangement is like that shown in Fig. 20 on page 74. A 0.1° thermometer is satisfactory for some experiments, but a calorimeter thermometer or Beckmann thermometer graduated to

0.01° is more desirable.   A Beckmann thermometer is adjusted to read near the bottom of the scale, otherwise the mercury thread may go above the top of the scale during the reaction.   Continuous, vigorous stirring is essential in all calorimetric measurements.   A stirrer of the propeller type, driven by a motor, is better than the hand stirrer.

A solution of $0.5N$ sodium hydroxide is prepared free from carbonate (page 446) and titrated against standard acid.   Solutions of hydrochloric acid and acetic acid slightly more concentrated than $0.5N$ are prepared by adding a drop or two of the concentrated acid to approximately $0.5N$ solutions.

Exactly 100 ml of the sodium hydroxide is pipetted into a dry vacuum bottle which is to be used as the calorimeter.   After rinsing the pipettes with hydrochloric acid, 100 ml of hydrochloric acid slightly more concentrated than $0.5N$ is run out of a second pipette into a second vacuum bottle, which has been previously rinsed with the same acid solution and drained.   In this way allowance is made for the solution adhering to the walls of the vacuum bottle when the acid is poured into the sodium hydroxide solution in the calorimeter.   Since the acid is slightly more concentrated, there is more than enough to neutralize the alkali and thus the exact amount is not important except as it affects the heat capacity of the solution.   After the experiment is completed, the solution should be tested with a drop of phenolphthalein.   If an alkaline reaction appears, the experiment is worthless because the acid is too dilute and the reaction is incomplete.

The Beckmann thermometer is set into the stopper, and the ring stirrer is adjusted so that there is no possibility of hitting and breaking the thermometer bulb.   The temperature registered should be near the bottom of the scale of the Beckmann thermometer.   The temperature of the acid solution is brought to that of the sodium hydroxide solution by inserting a small test tube filled with hot or cold water. When this tube is removed, it is allowed to drain while touching the side.   The same thermometer is used for both solutions.   It is allowed to drain while touching the side of the bottle and is then rinsed with water and wiped dry before inserting in the other vacuum bottle.

When the two solutions are brought to the same temperature within about 0.2° the acid solution is poured into the vacuum bottle containing the sodium hydroxide with rapid stirring and the time noted. An average of the two temperatures is taken as the initial temperature. The mixture is stirred constantly, and the temperature is read every minute for several minutes until the rate of temperature change becomes small and constant.

Check determinations are made on the heat of neutralization of hydrochloric acid and sodium hydroxide, and the average is used for calculating the heat capacity of the calorimeter.

In the same manner the heat of neutralization of acetic acid and sodium hydroxide is obtained.

Calculations.—The time-temperature curves are plotted, starting with the time of mixing. The nearly straight line that is obtained shortly after mixing is extrapolated back to the time of mixing, and the difference between this extrapolated temperature and the average initial temperature of the sodium hydroxide and the acid gives the temperature rise, corrected for cooling or heating from the room.

The heat q evolved in the reaction is equal to the total temperature rise Δt multiplied by the heat capacity l of the solution and s of the calorimeter. Thus,

$$q = (s + l)\Delta t \tag{1}$$

The heat capacities of the $0.5N$ solutions may be obtained from tables of specific heats and densities. The product of the density and the specific heat gives the heat capacity per milliliter of the solution. The resulting solutions of salts are $0.25N$ except for the change in volume on neutralization and the addition of the water of neutralization. The heat capacity of the products is obtained by multiplying the specific heat of the approximately $0.25N$ salt solution by the sum of the total weights of the reacting acid and base solution. The following data may be used at room temperatures:

SPECIFIC HEAT AND DENSITY OF SOLUTIONS

Solution	Specific heat	Density
$0.5N$ NaOH	0.968	1.021
$0.5N$ HCl	0.965	1.007
$0.5N$ H_2SO_4	0.975	1.009
$0.5N$ $HC_2H_3O_2$	0.999	1.003
$0.5N$ HNO_3	0.959	1.013
$0.25N$ NaCl	0.981	1.008
$0.25N$ Na_2SO_4	0.977	1.030
$0.25N$ $NaC_2H_3O_2$	0.963	1.034
$0.25N$ $NaNO_3$	0.956	1.012

The heat capacity of the calorimeter is obtained by introducing a known quantity of heat into the calorimeter and measuring the temperature rise. The heat of neutralization for $0.5N$ hydrochloric acid and $0.5N$ sodium hydroxide at $20°$ is 13,900 cal. At $25°$ it is

13,640 cal.   Then rearranging equation (1)

$$s = \left(\frac{q}{\cdot}\right) - l$$

If the heat absorbed per mole is equal to ΔH, and q is the heat evolved in the calorimeter by n moles then

$$n \tag{2}$$

where q is calculated by equation (1).

When the heat capacities of the reacting materials (hydroxide and acid solutions) are taken, the calculation gives the isothermal heat of reaction at the *final* temperature.   If the heat capacity of the products is taken, the calculated heat is the isothermal reaction at the initial temperature.[1]

The heat of neutralization for $0.5N$ acetic acid and sodium hydroxide is calculated from the experimental data and compared with the values found in tables.   The difference between the observed heat of neutralization and the heat of formation of water from H^+ and OH^- is due to hydration, incomplete dissociation, and other factors.

Practical Applications.—Measurements of heats of neutralization are of value in studying the properties of electrolytes.   This simple type of calorimeter is useful and adequate for the determination, with moderate accuracy, of the heat of most ordinary reactions in solution.

Suggestions for Further Work.—The heats of neutralization of other acids and bases may be determined.   Sulfuric acid, nitric acid, and ammonium hydroxide are suggested.   Heats of reaction of gelatin with sodium hydroxide and hydrochloric acid and other reactions of biological interest may be measured.   Heats of precipitation of barium sulfate and other insoluble materials may be determined. Nonaqueous solutions, such, for example, as the reaction of sodium alcoholate and hydrochloric acid in alcohol, may be studied.   The heats of mixing of two liquids such as alcohol and water, or partially diluted sulfuric acid and water, may be used to study the nature of the mixture and its departure from ideal behavior.

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24. Heat of Solution

The heat of solution of potassium nitrate in water is determined, using a vacuum-jacketed calorimeter with measured input of electrical energy to offset the cooling effect produced by the solution of the salt. The heat of solution may be correlated with the heat of dilution and with the temperature coefficient of solubility.

Theory.—This experiment is designed to illustrate the special advantage that endothermic reactions offer for calorimetric measurement. When the reaction absorbs heat, the cooling effect may be conveniently balanced with electrical heating in such a way as to involve no change in temperature. In this way, it becomes unnecessary to know the heat capacity of the calorimeter, and there is no need for an accurate thermometer. No cooling correction is necessary, and the method is simpler than the ordinary adiabatic method.

Many factors may be involved in the heat of solution, such as the heat absorbed in pulling apart the molecules or ions of the crystal, heat of combination with the solvent, and, in certain cases, heat of ionization. These quantities vary greatly with the specific nature of the solute and the solvent and with the concentration of the solution.

Considerable confusion existed in the early literature, because the difference between the differential and the integral heats of solution was not recognized. The *differential* heat of solution is the heat absorbed when a gram molecule of the solute is dissolved in a quantity of solution so great that the concentration is not appreciably increased by the addition of the solute. It may be determined by measuring the heat absorbed when small quantities of salt are dissolved in large quantities of solutions of different concentrations and plotting the heat absorbed against the concentration. A smooth curve is drawn through these points, and the tangent at any point gives the differential heat of solution at this concentration.

The *integral* heat of solution at a certain concentration is the heat absorbed when the solute is dissolved in the pure solvent to give a resulting solution of the specified concentration. In very dilute solutions there is no difference between the integral and the differential heats of solution, but in concentrated solutions there may be a large difference. The difference between the integral heat of solution at two different concentrations corresponds to the heat of dilution between these two concentrations.

According to the principle of LeChâtelier, those salts which, when dissolved, absorb heat must increase in solubility with an increase in temperature, and those which evolve heat must become less soluble at the higher temperatures.   The relation is put on a quantitative basis by the important equation of van't Hoff

$$\frac{d \ln S}{dT} = \frac{\Delta H}{RT^2}$$

where S is the solubility at the absolute temperature T, R is the gas constant, and ΔH is the heat absorbed when 1 mole of solute is dissolved in the saturated solution.

Apparatus.—Vacuum bottle; Beckmann thermometer, calorimetric thermometer reading 0.01°, or large bulb and capillary for reading constant temperature; stirrer (preferably electrically driven); electrical heating coil (enclosed in glass tube); sensitive ammeter (0.5 amp.); rheostat; 6-volt storage battery; switch; stop watch or electric clock; potassium nitrate; Wheatstone bridge.

Procedure.—The arrangement of apparatus is shown in Fig. 29. The heating coil of resistance wire is soldered to leads of heavy copper wire and enclosed in a U tube of glass.   Enough oil or kerosene is placed in the tube to cover the resistance wire, and the ends are closed with sealing wax.   The oil increases the heat conductance and prevents the circulation of overheated air.   Replacement coils for commercial heating units may be used.

The resistance of the heating coil is determined with a Wheatstone bridge, assuming that the resistance of the copper leads is negligible. An error is introduced because under the conditions of the experiment the wire is at a slightly higher temperature and the resistance is somewhat greater.

About 150 ml of distilled water is measured accurately and placed in the calorimeter A, the heating circuit is tested out by closing the switch and adjusting the rheostat so that the current is constant at 0.3 amp. or other suitable amperage, and the temperature is set close to that of the room.

The thermometer C may be a Beckmann thermometer, a calorimetric thermometer, or an improvised tube of mercury or toluene with a mark on the vertical capillary at the proper temperature.   Since the experiment is carried out isothermally, it is not necessary to measure a temperature difference.

About 2 g of potassium nitrate is weighed out to a milligram in the tube J and set in the calorimeter through the opening D, well below the water level.   The thermometer is watched while the water is stirred, and when the temperature becomes essentially constant the plunger

is pushed down, breaking the bulb and forcing the potassium nitrate out into the water. It is moved up and down to remove all the salt.

The cooling produced by the solution of the potassium nitrate is offset by closing the switch and allowing the electrical current to flow
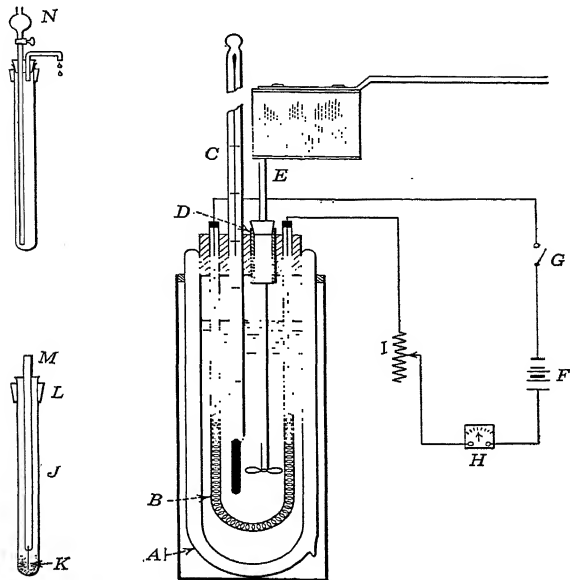
FIG. 29.—Calorimeter for heat of solution.

A. One-pint vacuum bottle containing about 150 ml of water.
B. Electric heating coil enclosed in glass tube.
C. Thermometer graduated to 0.01° (a large bulb blown on a capillary tube and filled with toluene may be used in its place).
D. Glass tube (1 cm diameter) with stopper for introducing tubes *J* or *N*.
E. Motor driven stirrer (a vertical ring stirrer operated by hand may be substituted).
F. 6 volt storage battery.
G. Electrical switch.
H. Ammeter for 0.5 ampere.
I. Rheostat for 0.5 ampere.
J. Tube with thin blown end for introducing solute, to be inserted through *D*.
K. Solute (2 g KNO₃).
L. Rubber collar for suspending solute tube *J* in calorimeter through *D*.
M. Rod with projecting point for breaking bulb, and forcing out solute.
N. Tube to be inserted in *D* for changing the temperature of the calorimeter by running through hot or cold water.

through the coil at exactly 0.3 amp. (or other suitable amperage) as regulated by the operation of the rheostat. The time of closing the switch is measured accurately with a stop watch, and the current is continued at constant amperage until the original temperature is restored. If the temperature falls after opening the circuit, owing to

the solution of more crystals, a second or third period of heating, accurately timed, may be necessary. When the experiment is finished, the thermometer must be exactly on the mark where it was at the beginning of the experiment.

Three or four successive determinations may be made, each one in a more concentrated solution of the potassium nitrate. Another determination is made in a solution nearly but not quite saturated with potassium nitrate.

Check experiments may be made with another filling.

Calculations.—The electrical energy E in joules is equal to the voltage multiplied by the number of coulombs. This energy is equal to the heat q absorbed by the dissolving solute because the final temperature is the same as the initial temperature. Neither the heat capacity of the solution nor that of the calorimeter enters the calculations. The number of coulombs is obtained by multiplying the current I in amperes by the total number of seconds t the current is flowing. The voltage is obtained by multiplying the current by the resistance R of the coil in ohms.

Then

$$E = I^2 Rt \text{ joules}$$

and

$$\frac{E}{4.183} = \text{heat in calories}$$

The data are calculated in terms of the number of moles of solute added per 1,000 g of solvent and the number of calories evolved per 1,000 g of solvent.

Then the total number of moles of salt contained in 1,000 g of water is determined after each addition of salt, by summing up the weights in all the determinations. In the same way the total heat evolved per 1,000 g of water is obtained by adding together the heat evolved per 1,000 g of water by each addition of salt.

A graph is then drawn in which the total heat evolved per 1,000 g of water is plotted against the concentration in moles per 1,000 g of water.

A tangent is drawn to the curve at two different concentrations and at infinite dilution. The slopes of these tangents give the differential heats of solution at the different concentrations. They are equal to $\frac{\partial q}{\partial n}$ where q is the total heat effect and n is the number of moles of solute.

Practical Applications.—The method described here is suitable for the measurement of most endothermic reactions. With a regular, sensitive thermometer it may be used for exothermic reactions, noting the temperature rise caused by the reaction, then cooling to the initial temperature and heating up through the identical temperature range by means of the electrical heating coil. It can be used also for the specific heats of pure liquids or solutions after first determining the heat capacity of the calorimeter with a measurement on pure water.

Suggestions for Further Work.—The heats of solution of urea may be determined as typical of a nonelectrolyte. About 5 g is taken instead of 2, but in other ways the procedure is the same as with potassium nitrate.

The heats of solutions of urea and of phenol are measured separately in water, and then the heat of solution of the compound $[(NH_2)_2CO]\cdot(C_6H_5OH)_2$ is measured. The heat of formation of the compound is then calculated.[1] The compound is prepared by fusing, in a test tube surrounded by boiling water, 9.40 g of phenol and 3 g of urea.

The heat of hydration of calcium chloride may be determined by measuring the endothermic heat of solution of $CaCl_2\cdot6H_2O$ and the exothermic heat of solution of $CaCl_2$.

The exothermic heats of solution and dilution of sulfuric acid may be determined.

The specific heats of salt solutions or organic liquids may be determined.

The solubility of potassium nitrate may be determined at 0, 20, 25, and 30°, saturating the solution with extra crystals at these temperatures and drawing out clear solutions with a pipette, covering the tip with filter paper held with a rubber band to prevent crystals entering the sample. The clear saturated solutions are then run out onto 2-in. watch glasses and weighed quickly to the nearest milligram. The four watch glasses are placed in a desiccator over sulfuric acid overnight and allowed to *evaporate* to dryness. The weight of the watch glass is subtracted from the weight of the watch glass and crystals after drying. The logarithm of the solubility in moles per 1,000 g of water is plotted against the reciprocal of the absolute temperature, and the slope multiplied by 2.303 is compared with the heat of solution in the saturated solutions determined with the calorimeter.

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CHAPTER VI

COLLOID CHEMISTRY

25. The Preparation and Properties of Colloids

Several shorter experiments of a more qualitative nature, designed to give some familiarity with the basic facts of colloid chemistry, are suggested. In each of the following experiments, the observations are to be recorded and hypotheses advanced to explain the observed phenomena.

1. Sol Formation (Suspensoid and Emulsoid Sols) (Typical).—Colloids may be produced by dispersion methods in which relatively coarse material is divided into finer particles, or by condensation methods in which molecules are gathered together into larger aggregates.

a. Ordinary potato starch is stirred in cold water and filtered through filter paper. Observations are made by testing the filtrate for starch. Another sample of the same potato starch is ground vigorously in a mortar for some minutes. The ground starch is now stirred into cold water and filtered as before. Any differences in behavior are observed and explained.

b. Half-gram quantities of a number of emulsification agents such as acetic acid, sodium lauryl sulfonate (Dreft can be used), egg albumin, lecithin, saforium, gum tragacanth, or gum acacia are each dissolved or suspended in 10 ml of oil of sesame, and 100 ml of water is added. Each mixture is passed through a portable hand homogenizer,* and tests are made to determine the stability (and foaming qualities) of the resulting emulsion.

c. Colloidal mercury is prepared by striking an arc between mercury electrodes under ordinary tap water. A simple glass apparatus such as is shown in Fig. 30 is suitable for the experiment. A small amount of mercury is poured into the funnel with a quartz tip. As the mercury drops away from the tip, the switch is closed to form the arc. The stability of the emulsion that is formed can be increased by adding a little potassium citrate (2.5×10^{-3} N) to the water.

d. Ten milliliters of 0.2 per cent auric chloride solution is made neutral with potassium carbonate solution. Small drops of an ether

* Suitable equipment is manufactured by the Club Aluminum Products Co., Chicago, Ill.

solution of yellow phosphorus (**Caution!**) are added to the gold solution, with constant shaking.   Care must be taken to avoid adding too much phosphorus.   The solution is examined by transmitted light and by reflected light.

To a very dilute cold solution of auric chloride, a small quantity of 1 per cent tannic acid solution is added.   The colloidal solution formed on boiling is very stable, owing to the protective action of the tannic acid.

To a solution of about 0.04 per cent auric chloride, a very dilute solution of hydrazine hydrochloride or phenylhydrazine is added, a drop at a time, with constant shaking.   Color changes are carefully observed.

e. Clean aqueous alcoholic solutions of certain proteins (gliadin, zein), resins, flowers of sulfur, etc., give colloidal suspensions upon addition of salt, alcohol, or water, or upon cooling. These techniques make possible fractional precipitations in poly-disperse systems because the larger molecules have lower solubilities.   Air-driven centrifuges are very effective in separating out and collecting the suspended material which causes opalescence.

2. Flocculation by Electro-lytes.—The addition of electro-lytes to a colloidal system causes

FIG. 30.—Arc for producing colloidal mercury.

changes in the stability of the system.   In coagulation by electrolyte addition, a significant quantity is the flocculation value, which is defined as the quantity of electrolyte per liter that is necessary to produce complete flocculation of the sol in some arbitrarily defined time.   It is the ion of opposite electrification that plays the major part in the process, and the valence of this ion determines the flocculation value.

One hundred milliliters of water saturated with hydrogen sulfide (hood) is added to 100 ml of water that has been boiled (5 min.) with

about 1 g of arsenious oxide and filtered.   The yellow solution is filtered, and the filtrate is examined with a beam of light for the Tyndall effect as shown in Fig. 31, which indicates the presence of colloids.

Five milliliters of $1M$ ferric chloride is allowed to fall, a drop at a time, into 200 ml of boiling water.   The solution now contains colloidal ferric oxide and hydrochloric acid.   The electrolyte may be removed by dialysis.   A membrane for dialysis is made by rolling a little collodion solution around in a large dry test tube until the surface is completely covered.   The excess collodion is drained out.   The upper edges are turned back as soon as the collodion is stiff enough.   After it has been standing for 5 or 10 min., water is poured into the tube and the membrane is worked loose from the tube.   The solution of colloidal ferric oxide and hydrochloric acid is placed in the dialyzer and set into a beaker of distilled water, and experiments are made to prove that the
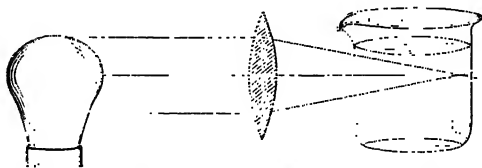
FIG. 31.—Diagram illustrating the Tyndall effect.

chloride ion diffuses through the membrane whereas the colloidal ferric oxide is retained.

To 10-ml portions of the colloidal arsenious sulfide are added small measured quantities of $0.1N$ sodium sulfate, $0.1N$ magnesium sulfate, and $0.1N$ aluminum sulfate, in order to determine what concentration of each is just sufficient to cause coagulation at the end of 5 min.   The relative efficiency of the different electrolytes is thus determined, although exact quantitative results cannot be expected.

The same experiment is repeated with colloidal ferric oxide and N sodium chloride, $0.1N$ sodium sulfate, and $0.1N$ disodium phosphate. Nonelectrolytes are also added to colloidal arsenious sulfide, ferric oxide, etc., in an attempt to coagulate them.

The ferric oxide colloid is mixed with an equivalent quantity of the colloidal arsenious sulfide.   The result is to be explained.

3. Von Weimarn Precipitation Law.—Insoluble compounds formed by the interaction of two dissolved substances can be made to precipitate readily or to form the disperse part of a colloidal system, depending upon the concentrations of the reacting substances in solution.   If the reactants are present in very low concentration or if they exist in

practically saturated solutions, colloidal suspensions are formed, for the rate of growth of the crystalline nuclei is slow in either case.

To 10 ml of $0.005M$ ferric chloride is added 10 ml of $0.005M$ potassium ferrocyanide. The solution is diluted with 5 or 10 volumes of water.

The experiment is repeated with $0.1M$ solutions and with saturated solutions, using small quantities.

4. Emulsion Types.—Two immiscible liquids and an emulsification agent are required for the formation of a stable emulsion. There are two emulsion types. Liquid A can be dispersed in B, or liquid B can be dispersed in A. If consideration is restricted to emulsions of oil and water, it is found that, in general, systems which preferentially adsorb anions in the interface or which have hydrophilic substances as emulsification agent favor the formation of oil in water systems. Conversely, water in oil systems are formed by cation interfacial adsorption or by organophilic emulsification agents.

Two milliliters of a 1 per cent solution of sodium oleate in water is placed in a 200 ml glass-stoppered bottle or flask, and benzene is added carefully with constant shaking. At first not over 1 ml at a time is added, but as the volume is increased more may be added. About 100 ml of benzene may be added. If too much is added at a time, the emulsion may "break," and a fresh start becomes necessary.

Ten milliliters of a benzene solution of magnesium oleate is placed in a 200-ml bottle, and water is added slowly, with vigorous shaking. About 40 ml of water may be added.

A drop of water is stirred into some of the first emulsion on a glass plate. A drop of benzene is stirred into another sample of the same emulsion. The experiments are repeated with the second emulsion. These tests show which liquid is the disperse phase and which is the dispersion medium, for the latter can mix with an added liquid, but the former cannot mix.

5. Gel Formation.—The coagulation of colloids does not always lead to precipitation, for it may result in the setting of the whole system to a gel. The study of the formation of gels is important because of its applications to industry and to the biological and soils sciences.

a. Fifty milliliters of $6N$ hydrochloric acid and 50 ml of sodium silicate solution of specific gravity 1.15 are placed in 200-ml beakers. The solutions are made up accurately and measured with an accuracy of 0.5 ml. The two solutions are mixed rapidly by pouring back and forth from one beaker to the other several times, after which the mixture should stand undisturbed. When the gel has set, the beaker gives

a musical ring when tapped.   Different sized beakers may be used for different tones.

After the gel has been standing still longer, the phenomenon of syneresis may be observed.   Water is squeezed out by the contraction of the gel, and the structure is broken.

Silica gel when dried possesses exceptional powers for the adsorption of gases.

b. To prepare a thixotropic gel, *i.e.*, one that shows isothermal, reversible sol-gel transformation, 3 ml of a 2 per cent sodium hydroxide solution is added to 30 ml of 5 per cent Iron Dialyzed (Merck) in an 8-in. pyrex test tube.   After thoroughly shaking the contents of the tube, the setting time is roughly 1 min.   Other gels may be formed to have longer or shorter setting times by varying the amounts of iron oxide and sodium hydroxide and by replacing sodium hydroxide with another electrolyte such as potassium chloride.

c. In rheopectic gels the setting time in the reversible sol-gel transformation may be reduced greatly by rhythmically tapping or rotating the container tube.   A thixotropic bentonite system which is also rheopectic may be prepared by dispersing the solid in water in the following manner.   A 5 per cent dispersion is prepared by slowly adding KWK Volclay bentonite* to the water with vigorous stirring to ensure uniform wetting.   An electric drink mixer or hand-operated egg beater is useful in the preparation of such dispersions.   After the dispersion has settled for several days, the unsettled portion is decanted. The decanted portion still should be 5 per cent in bentonite.   To 10 ml of this preparation in a 6-in. test tube, 1 ml of a 5 per cent sodium chloride solution is added slowly and with frequent shaking.   This forms a highly thixotropic system with very short setting time.   At this point 1 to 1½ ml of distilled water is added to the tube, carefully and drop by drop.   The purpose of this addition of water is to lengthen the thixotropic setting time.   When sufficient water has been added to lengthen the thixotropic period to 5 min., the gel shows a decided rheopectic behavior.

6. Interfacial Adsorption.—If there exists in a given boundary an energy potential that can be reduced by a change in concentration of solution toward the neighboring phase, solute will move into and sometimes across the interface.   The equilibrium constant in the interface differs from that of the bulk phase.   If the solute is a dyestuff like methyl violet, a color change may be produced by shaking the acid aqueous solution with an organic liquid.

* Volclay products may be obtained from the American Colloid Co., Chicago, Ill.

A little methyl violet is added to 0.5N hydrochloric acid. The colored solution is then shaken with benzene to give an emulsion, and the green color changes to violet. There is some doubt about the explanation for the color change, but it is supposed there is a deficiency of acid at the interface, the concentration of acid being lowered to such an extent that the indicator can change color.[6] Methyl violet changes from yellow to blue violet as the pH of the solution is changed from 0 to 2.

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26. Adsorption

Quantitative measurements of adsorption and their interpretation are here considered.

Theory.—Certain solids have the property of holding molecules at their surface. A loose chemical compound may be formed, or the attraction may be considered physical in nature. In either case, there is probably attraction between positive and negative charges. In many cases, at least, the layer of adsorbed molecules is only one molecule deep, and further adsorption ceases when the surface of the crystal lattice is covered.

The adsorption is greater at lower temperatures, and it depends on the nature of the adsorbing medium and the material adsorbed. In the case of solutions, it depends also on the solvent, and an equilibrium is set up between the material in solution and the material adsorbed on the surface of the adsorbent.

These qualitative facts find quantitative expression in the adsorption isotherm of Freundlich

$$\frac{x}{m} = kc^n$$

where x = the weight of material adsorbed by m grams of adsorbing material,

c = the concentration in solution.

n = a constant ranging from 0.1 to 0.5.

k = another constant.

Although k varies considerably with the temperature and nature of the adsorbent, the ratio of k for two different adsorbents is maintained in different solutions.

The equation of Freundlich is purely empirical in nature, and gives only the intermediate portions of the curve. The equation of Langmuir

$$a = \frac{\alpha c}{} \qquad \text{or} \qquad \frac{a}{c} = \alpha - \beta a$$

where a is the adsorbed quantity, c is the concentration, and α, β are constants, can be deduced, assuming a simple type of adsorption on the surface. This equation holds nicely in certain cases, at other times it gives results that are far from actual. The difficulty appears to be that there are a number of types of adsorptive forces, so that any equation which assumes a single type of simple nature cannot always account for the results of an experiment.

Apparatus.—Six 250-ml flasks; 2 burettes; N acetic acid; 0.1N sodium hydroxide; highly activated adsorbent charcoal (Norite); 100-ml volumetric flask.

Procedure.—Acetic acid solutions of different concentrations are made by running out N acetic acid from a burette and diluting to 100 ml with water; 50, 25, 10, 5, 2.5, and 1 ml are diluted with distilled water to 100 ml. Each solution is transferred to a 250-ml Erlenmeyer flask, and 1 g of adsorbent charcoal is then added to each flask. The solutions are allowed to stand an hour or more with frequent shaking or overnight if convenient. A thermostat is desirable but unnecessary if the room temperature is fairly constant.

When the charcoal no longer adsorbs acetic acid from solution, the flasks are allowed to stand until the charcoal has settled. A portion of suitable volume (5 or 25 ml, depending on the concentration) is pipetted out and titrated with 0.1N sodium hydroxide.

If possible, the determinations are repeated with a different variety of charcoal.

The experiment may be repeated, with oxalic acid instead of acetic acid.

Calculations.—The total weight of acetic acid in each solution is calculated from the data of the original solutions, and the titration gives the weight remaining in 100 ml of the solution after shaking with charcoal. The difference gives directly the weight of acetic acid

adsorbed by the m grams of charcoal ($m = 1$ g in the experiment described above).

The concentration c of the solution in equilibrium with the adsorbed acetic acid on the charcoal is calculated from the sodium hydroxide titrations, and the values of x/m are plotted against these equilibrium concentrations.

In case a parabolic curve is not obtained, the quantity of charcoal or the concentration is changed and the experiment repeated.

A second graph is constructed with $\log c$ plotted against $\log x/m$, and the best straight line is drawn through the points. The equation of this straight line is determined,

$$\log \frac{x}{m} = n \log c + \log k$$

and from it the constants n and k are evaluated for the equation of the adsorption isotherm

$$\frac{x}{m} = kc^n$$

It will be noted that the last equation is transformed into the preceding one by taking logarithms of both sides. The equations are only empirical, and the complete theoretical treatment is more complicated.

Practical Application.—The adsorption isotherm is important in the quantitative expression of the adsorption process, and as such it finds use in dyeing and in various purification processes. In a little different form, it is useful also for the adsorption of gases as well as for solutions.

Chromatic adsorption is finding application particularly in the separation of plant pigments. When crushed leaves are extracted with petroleum ether and poured through a tube of powdered sugar under the proper conditions, the different pigments are found to be adsorbed on the sugar at different levels. The sugar column is then separated into sections and dissolved.

Further material on chromatic adsorption is given by Morton.[6]

Suggestions for Further Work.—If the system is in equilibrium, the same results should be obtained whether approached from more concentrated or from more dilute solutions. Equilibrium may be tested by repeating the adsorption experiments and then diluting the solution with water after it has stood with the charcoal. Acetic acid should be given off by the charcoal to make the solution more concentrated, and the final values of x/m and c should still fall on the same curve.

Various other materials may be adsorbed—higher acids, or bases. Ammonium hydroxide is particularly suitable.

The adsorption isotherm may be tested nicely with dyes adsorbed on charcoal, the initial and final concentration of dye in solution being obtained with a colorimeter. The difference between the two readings gives a measure of the quantity of dye adsorbed by the charcoal. Methyl violet and malachite green are suitable dyes.

The adsorption experiments may be carried out at 0°C. and at elevated temperatures.

The values of the constants k and n are compared for the different materials and temperatures.

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27. Molecular Films on Liquids

The area of a monomolecular film is measured on the surface of clean water, and the cross section of a single molecule is calculated.

Theory.—The concentration and orientation of polar molecules in the surface of liquids are factors of vital importance in surface-tension and related phenomena. Langmuir, Harkins, Adám, and others have been able to show that, at an interface, such molecules are oriented in a definite manner, rather than at random. In addition, experience has led to the belief that films of insoluble substances on water are but one molecule thick. Thus, Frumkin has measured the surface saturation quantity of lauric acid on the surface of water and has found it to be 5.2×10^{-10} gram mole per square centimeter. Using the Gibbs adsorption equation,

$$\Gamma = -\frac{1}{RT}\frac{d\sigma}{d \log c}$$

the quantity Γ, which is the surface adsorption, was found to be 5.7×10^{-10} gram mole per square centimeter, a good agreement. The quantity $d\sigma/(d \log c)$, a surface-tension change with concentration, was determined by direct surface-tension measurements of lauric acid solutions, at several concentrations.

Langmuir suggested that in all cases, for both soluble and insoluble substances and for pure liquids, the film having special properties might be considered as one molecule thick. In the case of solutions having a surface tension lower than that of the solvent, the surface film would consist entirely of solute molecules. The area occupied by one

molecule A, assuming the film to be unimolecular in thickness, would be $1/\Gamma N$, where N is the Avogadro number. The development of the film balance by Langmuir, making it possible to measure the forces involved in the spreading of molecules over a liquid surface, did much to establish the theory of molecular orientation, for it afforded a sensitive and accurate differential method of measuring changes in the surface tension of the liquid. In this way, also, the forces required to compress surface films may be measured directly. The spreading of films on surfaces has been shown in this way to depend upon the shapes of the molecules and the relative activities of their different portions.

Apparatus.—Petri dish which has been scrupulously cleaned with hot sulfuric acid and potassium dichromate, or flat, rectangular glass dish with edges ground flat and coated with paraffine; powdered talc (in a salt shaker); strips of glass coated with paraffine; pure water; known amounts of organic chemicals, such as palmitic acid, stearic acid, oleic acid, myristin, laurin, stearin, palmitin, cetyl alcohol dissolved in benzene, ether, or other volatile solvent.

Procedure.—Devaux has suggested a convenient experimental method for the study of oil films, which is suitable for our purpose.
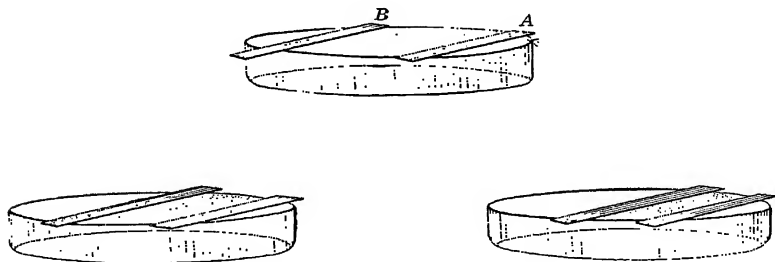
Fig. 32.—Molecular films on liquids.

The clean paraffined Petri dish (Fig. 32) is filled to overflowing with clean distilled water. In order to remove any possible further contamination from its surface, a little talc is dusted on the surface. The talc and impurities along with any excess water are then removed by the use of a strip of paraffined paper or clean glass strip A, which is moved with the thumbs all the way across the dish to the position C. A second paraffined paper or clean glass strip B rests on the surface of the clean water, at the opposite end of the tray. About five drops of oil solution obtained by dissolving a weighed amount of stearic acid in a known volume of benzene is then placed on the clean water surface

between the barriers. When the benzene has evaporated, a film made up of the solute molecules remains. If the concentration of the solution has been properly chosen (a solution that is 1 part per 10,000 by weight is recommended) the oil film will not completely cover the space between the barriers. After contraction of the film, which requires 15 or more minutes, the oil film is fanned gently into the region of the barrier A and the barrier B is moved in the direction of the barrier A, until the film just covers the area between the barriers. The oil-covered area may be distinguished from the water surface by dusting a small amount of talc on the surface. By fanning carefully on the surface, all the talc can be caused to collect on the oil film. The area of the oil film is then measured. It is important that several check determinations be made for each of the several substances used in the experiment.

The experiment is repeated with solutions of known concentration of other water-surface active molecules.

Calculations.—If the observed area is divided by the number of molecules of the polar substance on the surface, the cross-sectional area per molecule, on the surface of the water, is determined. The total number of polar molecules is readily obtained, when it is remembered that in one gram molecular weight there are 6.02×10^{23} molecules. The length of the molecules in the direction perpendicular to the surface is found as follows: By dividing the molar volume of the oil M/d by 6.02×10^{23}, the volume per molecule is obtained. By dividing this volume by the cross-sectional area of the molecule, the length of the molecule results.

The vertical distance between adjacent carbon atoms in the hydrocarbon residues of the polar molecules can be obtained by dividing the measured lengths of the molecules by the number of carbon atoms in the chain. X-ray measurements have shown that the nearest distance of approach of adjacent carbon atoms is 1.54×10^{-8} cm. These data make possible an estimation of the angle made by two carbon valence bonds.

Practical Applications.—The work of this experiment is important, because of its demonstration of the essential chemical nature of the forces involved in adsorption, surface-tension, and solution processes. It shows that the number of molecules of different fatty acids adsorbed per unit area is practically constant. Further, the configurations of other adsorbed molecules are of great influence in determining the number that can be adsorbed per unit area. Important information with regard to the structure of molecules is made available in this way. Perhaps most important of all is the conclusion that polar molecules in thin films and on surfaces are oriented. Studies of this kind are also of importance in connection with recent theories of emulsions and emulsification.

Suggestions for Further Work.—Relatively thin films of collodion can be obtained by allowing them to spread either on a cleaned mercury surface from ether-alcohol mixtures or on water from amyl acetate solution. Cellulose esters (celluloid, cellulose nitrate, etc.) can be spread on mercury surfaces from acetone solution. The area of the ultimate films of these materials depends somewhat upon the viscosity of the solution. Dilutions from 1 part in 1,500 to 1 part in 2,000 usually give satisfactory films. If the density of the material in the film form is the same as the ordinary density of the substance, the thickness of the film can be calculated. Cellulosic films may be as thin as 3×10^{-8} cm, but those of gelatin and other protein materials spread on alkaline water solutions are somewhat thicker.

In recent years Blodgett and Langmuir have developed and described simple techniques for the formation of multilayers. Built-up films of barium stearate on glass or metal have extremely interesting optical and mechanical properties, and thickness per layer and refractive index can be calculated with great accuracy.

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28. Film Balance

The pressure-area relations are determined for a thin film on the surface of clean water.

Theory.—The theory is discussed under Exp. 27.

In the prior experiment a known weight of spreading oil compound is dissolved in benzene and placed on the surface of clear water in a shallow dish. After the benzene evaporates, a film of oil is left which is confined between a movable barrier and a fixed barrier. The fixed barrier may be now changed to one that floats, provided that leakage of the oil film past its ends can be prevented. In the original film balance of Langmuir this was accomplished by air jets, but in more recent and improved forms of apparatus thin strips of aluminum foil are employed. In the film balance the force exerted by the film covering the area between barriers is measured by a lever and balance-pan arrangement or by a torsion-wire system which is attached to the center of the floating barrier. In this way the weight or torsional force required to bring this barrier back to the position it occupied in the absence of the oil film is determined. With the use of a rectangular

trough a differential apparatus is formed which records simultaneously the area and the tension of the oil film.

Apparatus.—Torsion-wire film-balance apparatus; purified volatile solvents; stearic acid, oleic acid, etc.

Procedure.—In the present day torsion-wire forms of film balance, the torque of the wire is calibrated by hanging a small balance pan from an arm attached horizontally and at right angles to the center of the wire and adjusting the torque for different weights placed on the pan. This is illustrated in Fig. 33. In some respects this calibration may be compared with that of the torsion on the wire in the DuNuoy surface-tension apparatus (page 28).
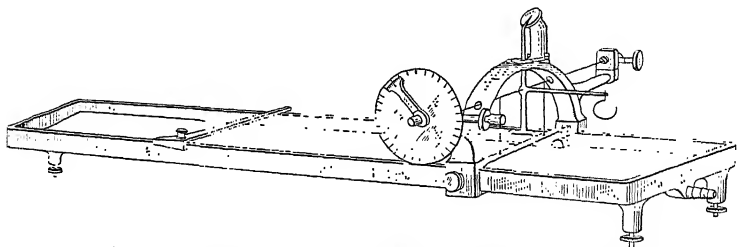
Fig. 33.—Balance for measuring the energy of surface films.

To perform an experiment, the cleaned trough is filled with distilled water and the surface is scraped clean with a strip of paraffined paper, clean glass, or mica slide. A calibrated drop (or drops) of an oil solution obtained by dissolving a weighed amount of stearic acid in benzene, 1 part per 1,000 by weight, is then placed on the clean water surface between the barriers. After evaporation of the solvent and contraction of the film the area of the oiled surface is altered by several changes in position of the movable barrier. With each change of position of the barrier, both the area of the film and the differential tension required to maintain the floating barrier in its position of equilibrium is observed. This floating barrier is usually constructed of mica. Talc is used to determine if the surface film is leaking around the barrier. This tension can be considered to be a two–dimensional pressure exerted on the film to keep it from spreading out indefinitely. Check determinations should be made. The work then may be extended to other benzene- or ether-soluble molecules.

Calculations.—A curve is plotted which shows the dependence of the differential tension or surface force exerted by the oil film on the

average area occupied by each molecule in the film. It will be seen that for relatively large areas the surface force is small, but as the area is decreased the force commences to increase, at first slowly and then extremely rapidly until the film collapses. If the curve in the region of sharply increasing surface force is extrapolated backward to zero compression, the limiting area per molecule is obtained. The force-area curve is a typical stress-strain diagram, and areas should be taken at zero stress to obtain a constant characteristic of the molecule in question.

It will be found that similar curves are obtained for series of long-chain saturated fatty acids, amides, alcohols, etc. In each case the extrapolated minimum area per molecule is practically constant at about 21 sq. Å. Interpretations of this fact and of the various regions of the force-area curve are to be given in the report. Resemblances between the behavior of gaseous films of the insoluble molecules (region of low differential tensions and large areas) and the pressure-volume relationships in the case of ordinary three-dimensional gases are especially worthy of note.

Practical Applications.—The film balance is now used for practically all quantitative work of this type directed toward the elucidation of molecular structure.

The technique of building multilayered films, developed by Blodgett and Langmuir, is finding important use in biology and medicine and in the production of birefringent plates. Built-up films of barium stearate are uniaxial crystals.

Research engineers of some electric-power companies use film balances to aid in explaining the electrical characteristics and degree of deterioration of transformer oils and oil-saturated wrappings of high-tension transmission cable.

Suggestions for Further Work.—In the experiment that has been performed, stearic acid is spread on neutral distilled water. In further work the effect produced on the spreading of stearic acid by making the water acid or alkaline may be studied. If the water is alkaline, the presence of minute traces of calcium, magnesium, and aluminum salts act to modify the spreading behavior.

Film-balance studies with lubricating oils that have been spread on a water surface offer interesting possibilities.

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29. Electrophoresis of Carboxyhemoglobin

Electrophoretic studies have several objects. They make possible the quantitative characterization of a substance by determination of the isoelectric point and mobility-pH and mobility-ionic strength relationships. In addition they may give important information about the homogeneity of a substance and aid in its isolation from a mixture of differently migrating materials. Thus the U-tube apparatus may be used for analytical or for separation experiments.

Theory.—The influence of the size and shape of particles on their electrophoretic mobilities has been the subject of much study. In the derivation of the classical mobility equation, the electrical double layer about the particle gives a system that may be likened to a condenser. The assumption is made that there are positively and negatively charged layers which are separated by a finite distance. The electrical force of the applied potential difference produces a displacement of one layer with respect to the other, with frictional forces of the particle in the dispersion medium opposing the displacement. At constant velocity, equilibrium between frictional and electrical forces is attained. Such considerations lead to the formula

$$u = \frac{\zeta H D}{4\pi\eta}$$

where ζ = the potential in the double layer.

η = the coefficient of viscosity of the medium.

H = the potential gradient.

D = the dielectric constant of the medium separating the layers.

u = the velocity of the particle.

This expression ignores the dimension of the particle but assumes it to be spherical in shape. In a given medium the mobility will depend upon the potential in the double layer. This potential is determined by the nature and condition of the surface of the particles. More recently Debye and Hückel have obtained a limiting formula for the mobility of spherical particles, which differs from the foregoing expression by the substitution of 6π for 4π. Henry and collaborators have made a theoretical investigation of this difference and conclude that the classical expression is valid provided that the radius of the particle is large compared with the effective thickness of the electrical double layer and that the electrophoretic mobility should vary with size, approaching the Debye-Hückel value for particles whose size is not large compared with the thickness of the double layer. As the experi-

ments are generally performed, and apart from the fact that they are nonspherical, the smaller soluble proteins should show an intermediate behavior.

Apparatus.—U tube graduated in milliliters; carboxyhemoglobin in buffer; phosphate buffer solution at pH 6, ionic strength 0.02; 110-volt d-c source.

Procedure.—The moving-boundary method for investigating electrophoresis has been so improved in recent years that it has become
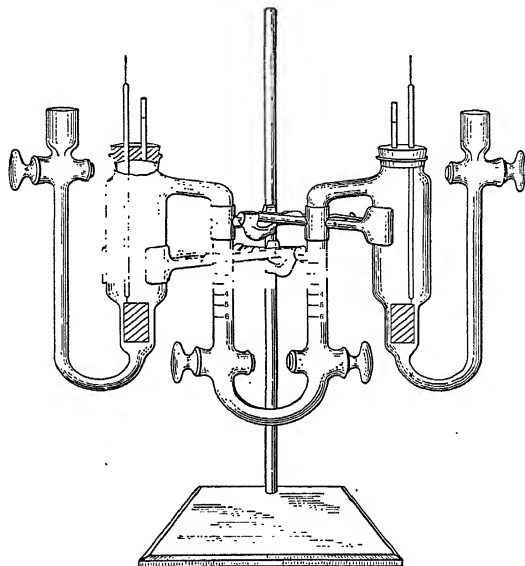
FIG. 34.—Apparatus for the electrophoresis of colloids.

extremely useful in the investigation of proteins and related colloids. The suspensions of most of these substances are colorless, and the position of the relatively diffuse boundaries must be followed by special optical methods that depend upon differences in light absorption or refractive index as the boundary is traversed. In this experiment we shall use as protein, carboxyhemoglobin to give a colored solution. The carboxyhemoglobin may be obtained from crystalline hemoglobin or prepared in relatively simple fashion by following directions given by Ferry and Green.[1] An extensive study of the electrophoretic behavior

of this system has been made recently by Davis and Cohn,[4] and we make use of many of their directions and observations.

A 1 per cent solution of the hemoglobin in phosphate buffer system at pH 6 is dialyzed in a cellophane bag against idential buffer for 1 or 2 days at about 4°C.   The purpose of this dialysis is to decrease disturbances at the protein-buffer interface.

The apparatus proper, a U tube which is connected by means of rubber tubing to large buffer chambers, is shown in Fig. 34.   The Ag–AgCl electrodes are immersed in 20 per cent potassium chloride solution.   The content of the U tube below the stopcocks is roughly 15 ml, that of the electrode reservoirs is 30 ml on each side, and that of the buffer chamber and vertical column of the U tube is of the order of 125 ml again on each side.   The diameter of the U tube is about 1 cm, and it is calibrated directly in milliliters.

The top of each buffer chamber is closed with a two-holed rubber stopper.   The second opening is for the introduction and leveling of the buffer solution.   For best results the several solutions should be freed from dissolved air by evacuation and brought to the temperature of the room just before the apparatus is filled.   In the U tube protein is layered under buffer solution, using the stop cocks for the separation. After making the rubber connections, buffer and salt solutions are introduced into the buffer chambers.[4]   After buffer solutions are carefully leveled in the tubes above the buffer chambers, the U-tube stopcocks are opened and buffer solution slowly added to one side and removed from the other until one hemoglobin column is raised into the optically uniform portion of the U tube above the stopcock.   A potential of 110 volts is applied to the electrodes, and the rate of movement of the protein boundary is obtained by direct visual observation. Observations of the protein boundary moving forward into buffer solution are more readily made because the boundary is sharp, but rates of migration taken from observations of the position of the receding boundary after definite intervals of time give more correct values of the mobility, in spite of the fact that these boundaries are more diffuse.

Calculations.—The mobility of the carboxyhemoglobin is calculated in units of cm/sec./volt/cm, or cm²/volt-sec.   Required are measurements of the rate of boundary migration, milliliters per hour, as observed; the specific resistance of the buffer; and the current through the system.   The mobility is

$$M$$

e rate of migration in milliliters/hour, K is the specific

resistance of the buffer solution, and i is current in amperes passing through the system.

Practical Applications.—Electrophoresis experiments give valuable information about the stability of both inorganic and organic colloids. Recently, electrophoretic methods have been applied with considerable success in the purification and characterization of proteins, and the application of the method to immune sera has given especially interesting results.

Suggestions for Further Work.—Observations on the influence of increasing pH and of increasing buffer ionic strength on the mobility of carboxyhemoglobin are of interest. At ionic strength 0.02 and pH 7.0 the mobility of the hemoglobin is nearly zero. If this pH is maintained and the ionic strength is increased, the direction of mobility is changed.

The use of ultramicroscopic electrophoresis cells has been developed by Abramson, Mattson, and others. These cells are especially useful in the study of the stabilities of inorganic colloids.

Another modification of electrophoretic analysis by the use of an M-shaped tube constructed of lucite has been described by Herriott, Desreux, and Northrop.

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30. Sedimentation Rate and Particle-size Distribution

The measurement of the velocity of sedimentation of particles in the earth's gravitation field or in a centrifugal field gives valuable information concerning their size. When the dispersed particles are so large that they exceed the limit of colloidal dimensions and when the density of the particle relative to that of the suspended medium is sufficiently great, they settle out under the force of gravitation. By measuring rates of sedimentation, particle size, and size distribution, determinations can be made with finely divided solids for which other sizing methods would be impractical or impossible.

Theory.—The constant velocity with which a spherical particle falls in a liquid may be expressed with a relatively simple law. The force of friction resisting the fall of the particle is $6\pi\eta r \dfrac{dx}{dt}$, and the force of gravity acting on the particle is mg, or $\frac{4}{3}\pi r^3 (d_p - d_m)g$. In these

expressions η is the viscosity of the liquid, r is the radius of the particle, dx/dt is the velocity of fall of the particle, d_p and d_m are the densities of the particle and of the suspension medium, m is the mass of a single particle, and g is the acceleration due to the earth's gravitational field. The force of gravity and the force of friction are exactly opposed and equal when the particle falls with constant velocity, and

$$- d_m)g$$

or

$$r = \sqrt{\frac{\overline{dx/dt}}{{}_p - d_m)g}} \tag{1}$$

This equation is known in the literature as Stokes' law.

Thus, if the sedimentation rate of spherical particles is measured, and the viscosity of the liquid, the difference in density between the particle and the liquid, and the constant of the sedimentation field are known, the particle size can be calculated. This statement is true for sedimentations in an ultracentrifuge as well as for ordinary sedimentations, and a very large number of determinations of the size of particles has been made by using the formula of Stokes. If the particles are asymmetric in shape, the exact particle size cannot be obtained in this way, but there may be evaluated an "equivalent radius" or the radius of an imaginary spherical particle of the same substance with the same observed velocity of sedimentation. The particle must possess some appreciable degree of asymmetry before this factor makes a marked difference in sedimentation rates.

Any ordinary powder consists of particles of many sizes. For such a powder the total range of particle size and the percentage of particles of a given size range can be determined by suspending the powder in a medium that wets it thoroughly and observing the accumulation times required for the powder to settle a given distance onto the pan of an analytical balance. Odén has used this general method successfully in the study of the distribution of size of particles of various coarse-grained sols such as soils, clays, and barium sulfate precipitates.

Apparatus.—Analytical balance; aluminum disk with $\frac{1}{4}$-in. flanged edge and wire suspension system; tall beaker; finely divided crystalline solids such as dolomite or crystalline quartz; precipitated barium sulfate.

Procedure.—In the preparation of the analytical balance for the performance of the experiment the left pan is removed and replaced by an aluminum disk with flanged edge and wire-suspension arrangement.

The suspension is formed by attaching three fairly heavy wires to the rim of the disk and connecting their apex by a small wire to the arm of the balance. The aluminum-disk balance pan is immersed to a known depth in water contained in a tall beaker, and the apparatus is balanced.

A water suspension of a weighed amount (about 5 g. solid to 10 ml of water) of crushed dolomite that has passed a 300-mesh screen is placed in a small crucible and inverted carefully at the surface of the water with a pair of tongs. In this way the dolomite particles have been thoroughly wet with water before the start of the sedimentation. During the manipulation the crucible should be inserted at the surface of the water. If the suspension is spilled from above, the particles will acquire an initial acceleration. The time at which the sedimentation begins is noted on a clock, and a stop watch is started. From time to time as the particles settle on the pan, weighings of the sediment are made. The weighings are continued until all the powdered dolomite has been collected. The length of time intervals between weighings depends upon the rate at which the sediment accumulates. Particles 5 to 40 μ in radius give suitable results in this experiment.

The experiment is repeated with finely divided quartz and with barium sulfate which has been precipitated in cold and in warm solution.

Calculations.—In this apparatus and procedure the largest particles settle at first and the sediment is an accumulation of particles graded as to size as contrasted with a mixture of particles of all sizes. For each time reading the radius of particles requiring that length of time to settle through the given distance is calculated from equation (1). Densities of the several solids are dolomite, 2.9; quartz, 2.65; barium sulfate, 4.5. If other solids have been used, their densities may be found in standard tables. Viscosity, velocity, and acceleration are all to be expressed in c.g.s. units for the calculation.

The weight of the powder settling in each time interval is determined and expressed in percentage of the total weight of material that has collected on the dish-shaped pan. The results of the experiment may be expressed in graphical form in which both particle radius and time of sedimentation are plotted against cumulative percentage of sediment.

The percentage of the powder or precipitate made up of particles having radii between two fixed values may be taken directly from the accumulation-time curve so that tables may be prepared to show what percentage of the powder has radii with values lying between each two successive particle-radius determinations.

For check determinations of the values obtained for the radii and for the distribution of radii of the particles, independent estimates of these quantities may be made by direct observation with a compound microscope provided with a micrometer eyepiece.

Practical Applications.—Knowledge of particle size and size distribution is finding important use in the cement, ceramic, ore-flotation, photographic-emulsion, and paint-pigment technologies. The rate of settling of precipitates is often important in analytical chemistry. Relationships between size and the behavior of soils, the stability of pastes, etc., have been recognized for a long time.

Suggestions for Further Work.—Sedimentation studies with typical soils, paint pigments, or cements may be carried out, and more complete mathematical analyses of the distribution curves may be attempted.

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CHAPTER VII

HOMOGENEOUS EQUILIBRIUM

31. The Dissociation of Nitrogen Tetroxide

This experiment gives experience in the determination of the degree of dissociation of a gas and the calculation of equilibrium constants.

Theory.—The reaction

is one of the simplest reactions for demonstrating the calculation of an equilibrium constant. The extent of the dissociation can be determined from the vapor density or from the depth of the brown color. Nitrogen dioxide is brown, and nitrogen tetroxide is colorless. The pressure is measured at various temperatures in a vessel of known volume; densities and the degrees of dissociation are calculated. An equilibrium constant is then calculated at each temperature.

Apparatus.—Special glass vessel with glass diaphragm; nitrogen tetroxide; mercury manometer; low-sensitivity galvanometer; high resistance; large beaker of water with heater and stirrer; thermometer.

Procedure.—Nitrogen tetroxide attacks mercury, stopcock grease, and rubber and therefore must be handled entirely in glass. The pressure of a corrosive gas may be determined by balancing against it a measured air pressure through a sensitive glass diaphragm, the point of balance being determined by an electrical contact (page 309).

The assembled apparatus is shown in Fig. 35.

The vessel is constructed from a 250-ml pyrex distilling flask with the addition of the glass diaphragm. It is filled with nitrogen tetroxide to a pressure of about half an atmosphere under conditions such that all air and moisture are removed, and then it is sealed off permanently. It is surrounded by a water bath adequately stirred and heated to a constant temperature with an electric heater, which is controlled by hand, or with a thermostat to give a constant temperature within 0.1° for at least 3 min. preceding the reading of the pressure and temperature.

The diaphragm has two platinum wires which close an electric circuit. One moves with a change in pressure and makes contact

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through a dry cell and high resistance (radio grid leak) and deflects a galvanometer of low sensitivity.

The tube leading from the diaphragm connects with a 4-liter bottle to act as a pressure buffer. The bottle is placed in a box, or it is wrapped in copper fly screen as a protection against flying glass in case of breakage. The bottle has three other tubes, one leading to the closed end manometer, one to the vacuum pump or water aspirator,
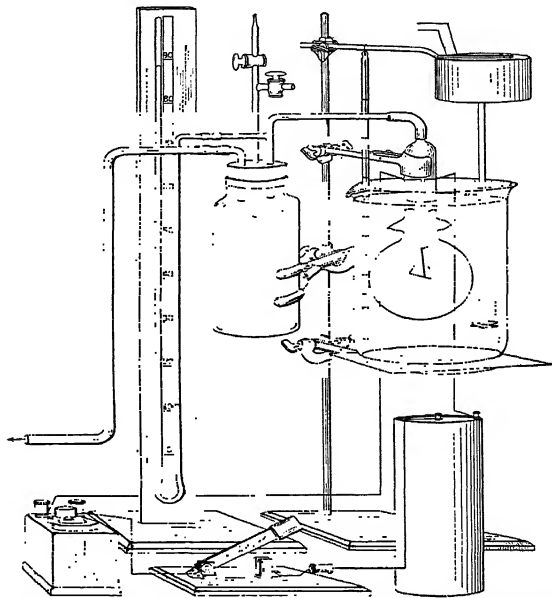
Fig. 35.—Apparatus for measuring the density of partially dissociated gaseous nitrogen tetroxide.

and one to a constricted tube, acting as a leak to the atmosphere to allow the pressure to build up slowly.

After the temperature has become constant, the stopcock is turned and the evacuation is continued until the galvanometer makes a sudden deflection indicating that the two platinum contacts in the diaphragm are touching. Evacuation should not be carried much beyond this point for fear of breaking the diaphragm or bending the wires. These diaphragms will stand much less pressure upward than downward. The stopcock is closed, and air is admitted slowly

through the leak. Just as soon as the galvanometer needle returns to zero, the stopcock is closed and a momentary opening of the evacuating stopcock will now cause the galvanometer to register. The manometer is read under conditions such that the electrical contacts are just touching.

The zero reading is the excess pressure on the manometer side over that in the flask which is necessary to just bring the contacts together and close the circuit. This reading depends on the angle at which the platinum wires are bent, and it may change with usage. It is taken very readily by removing the water thermostat and placing some carbon dioxide snow or a cake of dry ice against the bottom of the flask. Under these conditions all the nitrogen tetroxide is frozen out to a solid with a negligible vapor pressure. If all the air has been removed, the reading should be the same as if the flask were completely evacuated.

After taking the zero reading, additional pressure readings are taken at exactly 25° and at approximately 35, 45, and 55, and 15°. Check readings are taken at each temperature. To make sure that the zero point has not changed, it is advisable to determine the zero point again with dry ice after the other measurements have been taken.

The flask is filled with nitrogen tetroxide and sealed off for an indefinite number of experiments. The volume of the flask is first determined by filling to the points of constriction on the side arms with water run from a burette, or by weighing. The exact weight of nitrogen tetroxide is calculated backward from the known volume of the flask and the observed pressure at 25.0°.

The flask is filled the first time with the nitrogen tetroxide which is prepared by heating lead nitrate. A tube of pyrex glass approximately 10 mm in diameter and 50 cm long is closed at one end and filled with about 5 g of lead nitrate. It is clamped to a ring stand and heated with a Bunsen burner to drive out all water but not enough to give intense brown fumes. The water is wiped out or driven out by heating, and the end of the tube is bent into the form of a U. A little dry phosphorus pentoxide is placed in the bottom of the U, and the end is drawn out to a long capillary which is bent down, the open end being situated just above a layer of concentrated sulfuric acid or calcium chloride. The U part is set in ice and salt, and the end of the tube containing the lead nitrate is then heated intensely until most of the nitrogen tetroxide is driven over and condensed.

The liquid surrounding the phosphorus pentoxide should be light reddish in color. If it is greenish or muddy-colored, it contains some

water.   The capillary is broken off at the bend and inserted in one of the side arms of the gas flask and made tight with sealing wax.   The exit of the tube extends well beyond the sealing wax.   The U tube is cooled by touching with dry ice, and the flask is completely evacuated with an oil pump, while flaming with a Bunsen flame to remove all the adsorbed water.   The nitrogen tetroxide is allowed to melt momentarily to sweep out dissolved air, and then it is frozen again.   After evacuating for several minutes the side arm next to the pump is sealed-off at the constriction, and the nitrogen tetroxide is allowed to melt and build up to a predetermined pressure (half an atmosphere) as measured by the movement of the galvanometer.   The side arm holding the U tube of nitrogen tetroxide is then sealed off at the constriction, and the remaining liquid nitrogen tetroxide is retained for filling a second flask at a different pressure or for other purposes.

Two vessels may be prepared, one at a pressure of 200 or 300 mm and another at 500 or 600 mm, so that a liquid phase will form at the lower temperatures.

Calculations.—The apparent molecular weight of the mixture is calculated from the known volume and the measured pressure (page 3).   The total weight of N_2O_4 and NO_2 is calculated from the measured pressure, the known volume, and the accepted value for the dissociation constant K, at 25° as obtained from the literature.

The dissociation constant K_p is given by the following equation, where P represents the total pressure in atmospheres and α is the degree of dissociation:

$$K_p = \frac{p_{NO_2}^2}{p_{N_2O_4}} = \frac{\left(\dfrac{2\alpha}{1+\alpha}P\right)^2}{\left(\dfrac{1-\alpha}{1+\alpha}P\right)} = \frac{4\alpha^2 P}{1-\alpha^2}$$

The degree of dissociation α is defined by the equation

$$M_t - M$$

where M_t is the theoretical molecular weight (92) and M is the actually determined molecular weight.   If the dissociation were complete, M would be 46.

The value of K_p should come out practically the same with the two different vessels where the total pressures and the degrees of dissociation are different.   It changes slightly, however, with total pressure owing to deviations from the perfect gas laws.

The equilibrium constant K_p is calculated for each temperature, and an equation is determined which gives K_p as a function of T. This relation may be found by plotting log K_p against $1/T$ and finding the equation of the best line passing through the points (page 24).

The heat of dissociation ΔH is calculated by multiplying the slope of the line by 2.303 and the gas constant, 1.985 cal. per degree.

The free-energy decrease in the reaction, at a given temperature, may be calculated from the relation $-\Delta F° = RT \ln K$.

Practical Applications.—The determination of equilibrium constants is of fundamental importance in industrial work where the yield under specified conditions must be known. This experiment is typical for the study of many equilibria.

Suggestions for Further Work.—Other pressures may be used in addition to the two suggested.

Phosphorus pentachloride, ammonium chloride, and other reversible rapid decompositions can be studied at higher temperatures.

It is a good experience in technique to fill the vessels, and it is also good practice in glass blowing to make and mount the diaphragms.

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32. Equilibrium in Organic Liquids

This experiment illustrates the determination and calculation of equilibrium constants.

Theory.—An acid and an alcohol combine to form an ester and water; the ester hydrolyzes to give the acid and alcohol. The two opposing reactions proceed until an equilibrium is reached with all four compounds present in definite concentrations. The equilibrium constant K gives a measure of the relation between the activities of the products and the reacting materials. When the equilibrium constant has been determined, it is possible to calculate the yield that may be expected from any given concentration of reacting materials.

When concentrations are used in calculating the equilibrium constant, the equilibrium constant is in error on account of the failure of the mass law, particularly at high concentrations. An accurate value of the equilibrium constant is obtained by using activities instead of analytically determined concentrations. Activities may be determined by vapor-pressure measurements or by other methods. Details

are given by Lewis and Randall.[1] In many cases, however, the equilibrium constant may be calculated with fair accuracy from the concentrations.

The equilibrium is sometimes reached very slowly, particularly in organic reactions, and it may be necessary to raise the temperature or to use a catalyst.

The equilibrium between ethanol, acetic acid, ethyl acetate, and water is studied in this experiment, and the reaction is catalyzed by the addition of hydrochloric acid. Its concentration is great enough to change the character of the water and alter the numerical value of the equilibrium constant, but the results are fairly constant for a given concentration of hydrochloric acid. The hydrochloric acid is added merely as a catalyst to hasten the reaction, and it takes no part in the stoichiometric reaction.

Apparatus.—Burette; 5-ml pipette; 2-ml pipette; 1-ml pipette; six 50-ml glass-stoppered bottles; 0.5N sodium hydroxide; phenolphthalein, ethyl acetate, concentrated hydrochloric acid, glacial acetic acid, absolute ethanol.

Procedure.—A 3N hydrochloric acid is prepared by diluting concentrated hydrochloric acid. It is mixed with ethyl acetate and other materials in 50-ml glass-stoppered bottles, in the following proportions:

(a) 5 ml 3N HCl + 5 ml water.
(b) 5 ml 3N HCl + 5 ml ethyl acetate.
(c) 5 ml 3N HCl + 4 ml ethyl acetate + 1 ml water.
(d) 5 ml 3N HCl + 2 ml ethyl acetate + 3 ml water.
(e) 5 ml 3N HCl + 4 ml ethyl acetate + 1 ml ethanol.
(f) 5 ml 3N HCl + 4 ml ethyl acetate + 1 ml acetic acid.

Each of the bottles is stoppered immediately and allowed to stand a week, preferably in a warm place, with occasional shaking. It is necessary to have the stoppers fit tightly to prevent evaporation. A thermostat is unnecessary because this equilibrium is affected only slightly by temperature.

The weight of each material is determined by discharging the pipette directly into a glass-stoppered weighing bottle and weighing. In this way the following weighings are made:

5 ml 3N hydrochloric acid.
5 ml and 2 ml ethyl acetate.
1 ml ethanol.
1 ml acetic acid.
2 ml and 1 ml water.

The drainage of the pipettes will not always be uniform, but the error involved in using a pipette is not serious for the present work.

After standing a week, each solution is titrated with the $0.5N$ sodium hydroxide, using phenolphthalein as an indicator.

Calculations.—The original weight of ethyl acetate is obtained by weighing the liquid ethyl acetate discharged from the pipette (2 or 5 ml). The weight of acetic acid and ethanol in (e) and (f) is obtained in the same way. The weight of water is obtained by adding the weight of pure water to the water contained in the $3N$ hydrochloric acid. The latter is calculated by subtracting the weight of the hydrochloric acid, obtained by titration, from the weight of the 5 ml of hydrochloric acid solution.

The amount of acetic acid produced in the reaction is obtained by subtracting the number of milliliters of sodium hydroxide used in solution (a) from the number used for the final equilibrium titration. The former is a measure of the hydrochloric acid, and the latter is a measure of both the hydrochloric acid and the acetic acid. The difference, then, gives the amount of acetic acid produced. In (f), acetic acid is added to the original solution, and this amount must be subtracted from the amount calculated in the preceding manner. For every mole of acetic acid produced in the reaction, 1 mole of ethanol is produced, 1 mole of water disappears, and 1 mole of ethyl acetate disappears.

If the number of moles of each of the four materials in the original mixture and the moles of acetic acid produced in the reaction are known, the concentration in moles per liter of each material is readily calculated. The final volume is assumed to be 10 ml, although a slight change is caused by the mixing and by the reaction.

An equilibrium constant is calculated for each mixture, using the equation

$$K = \frac{c_{\text{CH}_3\text{COOC}_2\text{H}_5} \times c_{\text{H}_2\text{O}}}{c_{\text{C}_2\text{H}_5\text{OH}} \times c_{\text{CH}_3\text{COOH}}}$$

Practical Applications.—In planning any chemical synthesis, it is desirable to know what yield of material may be expected from a given concentration of reacting materials. Such a calculation may be made when the value of the equilibrium constant is known, provided that the reaction is fast enough to come to equilibrium in the time allowed.

Suggestions for Further Work.—Similar experiments may be carried out with other esters.

More significant results are obtained without the use of a catalyst, but under these conditions it is necessary to heat the mixture to about 150° in sealed tubes to effect an equilibrium within a couple of days. If sufficient precautions are taken to avoid danger from bursting tubes, the equilibrium constant may be determined by titrating mixtures that have been weighed out, sealed off in small glass tubes, and heated. The original work of Berthelot and St. Gilles[3] may be repeated.

The equilibrium involved in the reaction between acetaldehyde and alcohol to give acetal and water, using a little hydrochloric acid as a catalyst, may be followed by titration with sodium sulfite solution and thymolphthalein.[4,5]

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CHAPTER VIII

HETEROGENEOUS EQUILIBRIUM

33. Solubility as a Function of Temperature

Theory.—When a chemical system is in equilibrium, no apparent change takes place, but a dynamic equilibrium is assumed with two opposing reactions proceeding at the same rate. One of the simplest cases of equilibrium is that of a saturated solution, in which molecules leave the solid and pass into solution at the same rate at which the molecules in solution are deposited on the solid. The solubility of a solid, *i.e.*, the concentration in a saturated solution, is then a special case of an equilibrium constant.

The relation between an equilibrium constant and the absolute temperature developed by van't Hoff is one of the most important equations in chemistry. An equilibrium constant enables one to predict how far a chemical reaction will go; it can be calculated for any temperature when it is known at two temperatures.

The mathematical relation is

$$\frac{d \ln s}{dT} \qquad \frac{\Delta H}{RT^2} \tag{1}$$

and in the integrated form

$$\log s = \frac{-\Delta H}{2.303R} \frac{1}{T} + C \tag{2}$$

or

$$\log \frac{s_2}{s_1} = \frac{\Delta H(T_2 - T_1)}{2.303R(T_2 T_1)} \tag{3}$$

where s_2 and s_1 are the solubilities, in moles per 1,000 g of solvent at the absolute temperatures T_2 and T_1, R is the gas constant, and ΔH is the heat of solution per mole. In this integration ΔH is assumed to be constant, an assumption that is not entirely justified.

The heat of solution is the heat absorbed when 1 mole of the solid is dissolved in a solution that is already practically saturated. It differs from the heat of solution at infinite dilution, which is the heat

of solution usually given in tables, by an amount equivalent to the heat of dilution.

Apparatus.—Water bath regulated for 30°, 25°, and 20°; ice bath at 0°; large test tube; 0.05N sodium hydroxide; benzoic acid or boric acid; 0.1° thermometer; 10-ml pipette; 10-ml weighing bottle.

Procedure.—The solubility of benzoic acid is determined at 30, 25, 20, and 0°, or at other convenient temperatures below room temperature; the temperature is read to 0.1°, with a thermometer immersed in the solution.

Distilled water in large test tubes is saturated with benzoic acid by dissolving crystals at a higher temperature and then cooling to the required temperature so that some of the dissolved material is crystallized out. When the equilibrium is approached in this way from the molecular side, rather than from the crystal side, the equilibrium is attained rapidly. Hours or sometimes days may be required to reach an equilibrium when the passage of molecules across a boundary between two phases is involved. For the same reason, if the thermostat is not constant, a falling temperature may not be serious, but a rising temperature may introduce a considerable error.

The solution is stirred for about 15 min. with a ring stirrer safely enclosing the thermometer in such a way that the bulb cannot be broken and operated vertically by hand until the temperature is constant. A figure is shown on page 90. A simple thermostat improvised from a large beaker and a stirrer driven by a motor or compressed air may be used, for temperature control of 0.1 or 0.2° for 15 min. or so is sufficient. A 10-ml sample is removed with a pipette, drained into a weighing bottle, and weighed to 0.01 g. A piece of filter paper is attached over the tip of the pipette for filling, to prevent the entrance of small crystals along with the sample, but it is removed for draining. The solution is then titrated with 0.05N sodium hydroxide.

Duplicate determinations are made at each temperature.

Boric acid may be used instead of benzoic acid for this experiment. It is titrated by using phenolphthalein as an indicator and adding 10 to 20 ml of neutralized glycerin to give a sharp end point.

Calculations.—The solubility in moles per 1,000 g of solvent is calculated at each of the four temperatures and compared with the accepted values. It is interesting to compare these values with the solubilities calculated as moles per liter.

The logarithm of the solubility in moles per 1,000 g of solvent is plotted against the reciprocal of the absolute temperature, and a smooth curve is drawn through the four points. If the heat of solution

were constant and there were no complicating reactions, such as ionization, the line would be straight. Tangents are drawn at 25° and at 0°, and the heat of solution is determined at the two temperatures with the help of equation (2).

Equation (3) is used also to calculate the heat of solution, and then to calculate the solubility at a different temperature. For example, the solubilities at 25° and 30° may be taken for calculating ΔH, and then using ΔH and the solubility at one temperature, the solubility at 20° may be calculated. This solubility is then compared with the experimentally determined solubility.

Practical Applications.—The solubility of a substance may be calculated at other temperatures when it has been determined at two different temperatures. The results are more accurate when the heat of solution is not affected by temperature or when the temperature range is small.

Many other equilibria, such as vapor pressures or chemical reactions, can be calculated in the same way.

Suggestions for Further Work.—The solubility of other materials may be determined in a similar manner. Oxalic acid or some other substance that can be easily titrated in solution is suitable. The very soluble materials are not suitable. Nonaqueous solvents may be used also.

The heats of solution thus determined may be compared with the heats of solution determined calorimetrically (page 107).

In equation (2) it is assumed that the heat of solution is independent of temperature, but this assumption is not often justified. The equation may be made exact by introducing terms for the heat capacity of the solute and solvent and for the solution.

The influence of salts in reducing the solubility of benzoic acid may be determined.[5] The salting-out constant thus obtained can be used for calculating activity coefficients.

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34. Distribution of a Solute between Immiscible Solvents

Quantitative measurements are made of the amount of a solute extracted by an immiscible solvent. Any association or dissociation of the solute is determined.

Theory.—When two immiscible solvents are in contact with each other, a dissolved substance will distribute itself between the two, according to a definite equilibrium. The phenomenon is analogous to that of a dissolved gas distributed between a gas space and a liquid, and the mathematical treatment is similar to that of Henry's law. As in most cases of equilibrium, the kinetic explanation is satisfactory. When the rate at which the molecules of solute pass from the first solvent to the second is equal to the rate at which they pass from the second to the first, a dynamic equilibrium is set up, and no further change in concentration occurs. The ratio of the concentrations in the two solvents under these conditions, c_1 and c_2, gives the distribution coefficient (or partition coefficient)

$$K = \frac{c_1}{c_2} \tag{1}$$

If association of the solute occurs in the second solvent, the simple ratio as given in equation (1) does not yield a constant, because a second reaction is involved

$$(c_2)_n = n(c_2) \tag{2}$$

and the corresponding equilibrium constant K_2 for the association is

$$K_2 = \frac{(c_2)^n}{(c_2)_n} \tag{3}$$

The *distribution* is concerned with only one type of molecule, but the chemical analysis does not distinguish between the single molecules and the associated ones.

When $n = 2$, the concentration of the unassociated form is proportional to the square root of the concentration of the associated form and equation (1) becomes

$$K' = \frac{c_1}{\sqrt{c_2}} \tag{4}$$

Similar considerations apply when the solute is dissociated as well as when it is associated.

If the association is not complete, n is not a whole number. When the association or dissociation changes appreciably with concentration, it is necessary to include the degree of dissociation or association at each concentration.

The carboxylic acids are suitable for a study of this type because they generally form double molecules in nonpolar solvents or in the

gas phase, but these are broken down into single molecules in polar solvents such as water. Some carboxylic acids such as acetic acid are so weak that their ionization in water can be practically neglected, but others such as chloroacetic acid are almost entirely ionized.

Apparatus.—Three 100-ml separatory funnels; three 100-ml Erlenmeyer flasks; 100-ml volumetric flask; 25-ml pipette; 10-ml pipette;. $1.0N$ acetic acid or trichloroacetic acid or other acid; carbon tetrachloride; ether; carbon dioxide-free water (page 159) $0.1N$ sodium hydroxide, and $0.01N$ for carbon tetrachloride.

Procedure.—One hundred milliliters of $1.0N$ acetic acid is diluted with an equal volume of carbon dioxide–free water; and 100 ml of this solution is diluted again with an equal volume of water, giving $0.50N$; and $0.25N$ acetic acid. Twenty-five milliliters of each of the three solutions is pipetted into closed 100-ml separatory funnels, and to each is added 25 ml of carbon tetrachloride. Closed rubber tubes are put over the outlets to keep out the water from the thermostat, and the separatory funnels are set in a thermostat at 25° for 20 min. or more with frequent shaking.

A second set of experiments is carried out in the same way, using 25-ml samples of ether instead of carbon tetrachloride.

After the solutions have come to equilibrium, the separatory funnels are removed and the lower layers run out into a beaker, care being taken to let through none of the upper layer. Ten-milliliter samples of each are taken rapidly to avoid evaporation and run out into Erlenmeyer flasks for titration with the sodium hydroxide, using phenolphthalein as an indicator. Samples of the upper layers are removed from the separatory funnels with 10-ml pipettes, care being taken to avoid sucking up any of the lower layer.

Check titrations should be made in each case.

The sodium hydroxide is standardized against standard acid, and the titrations should be made quickly to prevent absorption of carbon dioxide from the air. In titrating the acid dissolved in carbon tetrachloride or ether, it is necessary to shake vigorously to accelerate the passage of dissolved acid across the surface and into the water layer.

The effect of successive extractions may be studied. Fifty milliliters of the $1.0N$ acetic acid is shaken with 25 ml of ethyl ether in the thermostat, and the ether layer is carefully run off at the bottom, allowing none of the aqueous solution to escape. Samples of 10 ml are titrated as before, and the amount extracted by the whole 25 ml is calculated. The remaining water solution is again shaken with a second 25-ml portion of ether. This time the ether layer and water layer are both analyzed.

Calculations.—The concentrations of acid in the two layers are calculated in moles per liter to obtain constants with absolute values so that they can be checked with the work of other investigators. It is obvious that this calculation to moles per liter is not necessary in the case of equation (1). The distribution ratio is calculated, using various formulas until one is found that will give about the same value for K at all the different concentrations.

The amount of acetic acid extracted by adding an equal volume of ether to the aqueous solution of acetic acid is calculated and compared with the amount extracted when the same volume of ether is used in two successive extractions, using half the volume of ether each time. A formula may be developed that shows how the efficiency of extraction depends on the number of portions, n, into which the given volume of extracting solvent is divided.

Practical Applications.—Extraction of a solute by shaking a solution with another immiscible solvent is an operation that is used extensively in organic chemistry. The efficiency of the operation may be calculated when the distribution coefficient is known.

The escaping tendency of a solute determines its distribution into a second solvent, and the effective concentration, or the "activity," of the solute may be calculated from distribution data.[1]

The effective concentration may be determined without disturbing the equilibrium in the solution. For example, in a solution containing iodine dissolved in a solution of potassium iodide,[1] the amount of free iodine cannot be determined by titration, because, as soon as iodine is removed, the potassium tri-iodide which is present in solution dissociates and keeps up the supply of iodine. The solution may be shaken with a little carbon tetrachloride, and the free iodine distributes itself between the two liquids. The concentration of iodine in the carbon tetrachloride layer may be determined without the complication of the potassium tri-iodide compound; the concentration of free iodine in the aqueous solution may be obtained by multiplying the concentration in the carbon tetrachloride solution by the distribution ratio between carbon tetrachloride and water.

Information concerning the extent of dissociation or association of a solute may be obtained by distribution measurements.

In some cases, the degree of hydrolysis of a salt may be determined by measuring the distribution ratio of the acid or base when shaken with an immiscible solvent.

Suggestions for Further Work.—Other distribution systems may be studied, such as the following:

Hydrochloric acid between water and benzene.[3]

Salicylic acid between water and benzene, and between water and chloroform.

Picric acid between water and benzene.[4]

Iodine between liquid benzene and solid benzene.

The iodine distribution between potassium iodide solution and carbon tetrachloride may be determined.

The extent of hydrolysis of a salt, like aniline hydrochloride, may be determined.

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35. Transition Temperature

In this experiment the determination of a transition temperature between various crystals is illustrated by three different experimental methods.

Theory.—When a substance changes from one crystal form into another, the change is accompanied by an absorption or evolution of heat and by other phenomena such as change in vapor pressure, volume, or color. The temperature at which such a change takes place is called the "transition temperature."

The temperature at which a change of phase takes place may be determined in a number of ways. One of the most common methods consists in determining a cooling or heating curve in which temperature is plotted against time. Thus, for example, if water is cooled sufficiently, its temperature will fall continuously until 0°C. is reached. After staying at 0° until all the water has frozen, the temperature will again continue to fall. The heat evolved on freezing counterbalances the heat lost by radiation and maintains the system at the freezing temperature as long as any liquid water is left.

The transition temperature of sodium sulfate is to be studied. This is the temperature at which hydrated sodium sulfate is in equilibrium with the anhydrous form.

$$Na_2SO_4 \cdot 10H_2O \rightleftarrows Na_2SO_4 + 10H_2O$$
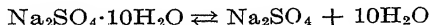
Under these conditions there are two components and four phases, and according to the phase rule there are no degrees of freedom. There is, then, one temperature and only one at which anhydrous sodium sulfate, hydrated sodium sulfate, solution, and vapor can exist together. This temperature is 32.383°C., and it is just as definite as the freezing temperature of water under conditions where there are one component and three phases.

Apparatus.—Two large test tubes; 0.1° thermometer, 0 to 50°C.; stirrer; anhydrous sodium sulfate; hydrated sodium sulfate; dilatometer filled with sodium sulfate and saturated solution, and provided with a 0.1° thermometer.

THERMOMETRIC METHOD

Procedure.—An 8-in. test tube is set into a larger one which serves as an air jacket as shown in Fig. 25.   A thermometer, graduated to 0.1° and reading from 0 to 50°, is fitted into a cork in the mouth of the smaller test tube.   A vertical stirrer is made by bending a piece of glass rod of small diameter into a ring surrounding the thermometer. Care must be taken that the stirrer is so constructed and the thermometer so placed that the thermometer bulb cannot be broken when the stirrer is operated.

Hydrated sodium sulfate is mixed with a little anhydrous sulfate. The latter may be prepared from the former by allowing it to effloresce by standing in the air.   The inner tube is filled and heated to 34 or 35°, inserted in the outer jacket, and set into a beaker of water at room temperature.   The solution is stirred continuously, and the temperature is recorded every minute or so.   Temperature readings are plotted against time.

The straight part of the curve near 32.4° is of interest.   It is unnecessary to take extensive readings before and after this part is reached.   If the temperature drops so slowly as to prolong the experiment unduly, the tubes may be set into colder water.   If the temperature falls much below 32.4° without becoming constant, the solution has become supercooled, and a crystal of hydrated sodium sulfate should be dropped into it.

Impurities in the salt or inaccuracies of the thermometer may introduce errors.   To eliminate the first source of error, the sodium sulfate is crystallized until two successive crystallizations give the same transition temperature.   Usually one or two crystallizations are sufficient.   The salt may be crystallized readily by forming a saturated solution in distilled water at about 30° and cooling to 0° in an ice bath. The crystals may be dried conveniently on a Büchner funnel attached to a filter pump.   The last mother liquor may be squeezed out effectively by placing a piece of thin rubber sheet over the rim of the funnel in such a way that the atmospheric pressure forces the rubber down against the crystals.

The zero point of the thermometer is checked in an ice bath.

Calculations.—Curves are plotted, with time on the X-axis and temperature on the Y-axis.   When the transition temperature remains unchanged after successive recrystallizations, the salts may be con-

sidered pure, and the horizontal part of the curve may be taken as 32.383°C.

The correction for the thermometer at 0° is calculated from the reading in the ice bath.

DILATOMETRIC METHOD

Procedure.—The dilatometer shown in Fig. 36 may be constructed from a small flask or a large test tube to which is fused a ground-glass joint. A 0.1° thermometer is set into the inner joint with sealing wax. The capillary side arm is about 20 cm long and has a bore of about 0.5 mm. A millimeter scale is attached, with sealing wax or other material. The scale may be scratched on and the marks filled with glass marking ink. The lower half of the flask is filled with hydrated crystals mixed with unhydrated crystals, and the stopper with the thermometer is inserted carefully so as to force out any air bubbles. The thermometer bulb should be near the center of the vessel.

The dilatometer containing the solution and crystals is placed in a larger beaker of water provided with an efficient stirrer and very gradually heated from about 31 to 34°. At frequent intervals (every minute or so, depending on the rate of change) the level of solution in the capillary is recorded, together with the temperature. After holding at a constant temperature of about 35° until there is no further change of level in the capillary, the temperature is allowed to fall back very slowly to 31° and again the readings of the capillary and the thermometer are taken.

Calculations.—The capillary heights, which represent the volume of solution and crystals, are plotted against temperature, for both the rising and the falling temperatures. The changes in volume are due to changes in solubility and density, but at the transition temperature there is an

Fig. 36.—Dilatometer for solids.

additional large change due to a change in the crystal form. The curves will be irregular owing to changes in the rate of cooling but the important thing to notice is the abrupt change of volume, indicating the transition temperature. This temperature, determined

by the volume change, is to be compared with the transition temperature obtained thermometrically.

SOLUBILITY METHOD

Procedure.—The solubility of sodium sulfate in moles per 1,000 g of water is as follows:

	$Na_2SO_4 \cdot 10H_2O$			Na_2SO_4			
Temperature.............. 0	20	25	30	32.38 35	40	45
Solubility................ 0.342	1.33	1.9	2.8	3.50 3.45	3.40	3.28
(moles/1,000 g)						

If time permits, some of these solubilities may be verified by maintaining the saturated solution at a given temperature for 5 min. with stirring and then discharging a 10-ml pipette full of the clear solution into a small weighed crystallizing dish or evaporating dish and weighing the solution to 0.1 g.   The solution is evaporated to dryness, dried in an oven at 100 to 105°, cooled in a desiccator, and weighed to 0.01 g.

A few perfect crystals of hydrated sodium sulfate are dried with filter paper and weighed quickly.   They are heated at 100 to 105°, cooled in a desiccator, and weighed.   The heating is repeated until a constant weight is obtained.   The number of moles of water per mole of sodium sulfate is calculated for the hydrated crystals.

The crystal form of both hydrated and anhydrous sodium sulfate is examined, using a lens or low-power microscope.   Sketches of each are made, and the class to which each crystal form belongs is specified.

Calculations.—A graph is drawn showing the solubility plotted against the temperature, using the data given in the table, together with any points determined experimentally.   There are two solubility curves, one for the anhydrous salt, the other for the hydrated salt, and the intersection of the two curves gives the transition temperature. This value for the transition temperature is compared with those obtained by the thermometric and dilatometric methods.

The possible phases are solution, vapor, Na_2SO_4, and $Na_2SO_4 \cdot 10H_2O$.   The phases present at each area, line, and point in the diagram are specified, and the number of degrees of freedom are calculated by the phase rule.

Practical Applications.—The transition temperature having been determined, it is possible to control the product that crystallizes out.   Below 32.383° the hydrated form crystallizes out, and above 32.383° the anhydrous form is obtained. Considerations of this kind are important in the production of many salts on a commercial scale.

The transition temperatures of salts are used in standardizing thermometers. Sodium sulfate is the most commonly used substance, because the temperature is fairly close to room temperature and because the salt can be easily purified.

Transition temperatures are also used to give a warning when a bearing becomes overheated. The bearing is painted with a paint that contains a substance giving a decided change in color when the transition point is exceeded. Other hydrated salts are listed on page 420.

Suggestions for Further Work.—The colorimetric method, which is perhaps the most obvious, may be illustrated with cuprous mercuric iodide ($2CuI \cdot HgI_2$), which changes color at 67.5°C. The transition from one solid phase to another in the absence of a solution is very slow, and the time lag is sufficient to cause errors of several degrees. A little cuprous mercuric iodide is placed in a thin melting-point tube and attached to an ordinary thermometer. On heating very slowly in a small beaker of water, the color change may be detected. The reverse change is observed when the water is cooled very slowly. The average of several determinations is taken as the transition temperature, and the agreement is better, the slower the change in temperature.

Transition temperatures may be determined also by locating the point of intersection of two vapor-pressure curves. At the transition temperature, both forms are in equilibrium and they must have the same vapor pressure.

The transition temperature of sulfur may be obtained by determining the solubility curve of monoclinic and rhombic sulfur in nitrobenzene between 80 and 120°.

Transition temperatures may also be determined by the use of potentiometric and conductance methods.

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36. Freezing-point Diagrams

This experiment is like the preceding one, in that it illustrates the use of cooling curves in determining the temperature at which one phase passes into another. It illustrates also the use of the thermocouple.

Theory.—The purpose of the experiment is to obtain experimental data by "thermal analysis" for constructing a phase diagram, which indicates the solid and liquid phases that are present at each temperature and concentration. The concentrations are made up arbitrarily, and the temperatures at which solid phases appear are indicated by irregularities in the cooling curves. A slower rate of cooling is obtained during the change in state because the heat evolved by solidification partly offsets the heat lost by radiation and conduction to the colder surroundings.

Apparatus.—Six small crucibles, containing tin, lead, and their binary mixtures; thermocouple and potentiometer; Méker burner; asbestos-lined can for slow cooling

of the crucible; crucible tongs; small thin tubes of iron; small crucible containing bismuth; watch, or electric clock; vacuum bottle.

Procedure.—The thermocouple, of copper-constantan or alumel-chromel, is connected to the potentiometer (pages 189 and 371) and standardized from readings made in boiling aniline (184°), freezing tin (232°), freezing bismuth (271°), or in freezing lead (327°), as described on page 426. The cold junction is placed in ice in a vacuum bottle.

Six narrow crucibles are filled with the following:

1. Lead, 80 per cent; tin, 20 per cent.
2. Lead, 60 per cent; tin, 40 per cent.
3. Lead, 40 per cent; tin, 60 per cent.
4. Lead, 20 per cent; tin, 80 per cent.

Pure tin and lead are also used unless they have been used already in obtaining the calibration curve. A thin layer of fine graphite is placed over the metals and alloys in the crucibles to minimize oxidation.

Each crucible, containing one of the metals or mixtures of metals, is heated, until the mixture is *just melted*. If the crucible has been heated above the temperature of complete melting, oxidation will be more serious. Moreover, a large number of readings of no value will then be required at the beginning of the experiment. The crucible is then transferred to a small can, which is covered with asbestos, and allowed to cool slowly. Pure substances show but one freezing point, whereas most mixtures show two. After the freezing points have been reached, it is unnecessary to continue the readings much farther along the cooling curves. The end of the thermocouple must be well immersed in the molten bath.

A small iron tube, closed at the bottom, is placed in each mixture. One end of the thermocouple is placed in one of these tubes and insulated. Care is taken to prevent contamination; a tube from one crucible is never set into another. The cold end of the thermocouple is kept in a tube in an ice bath contained in a vacuum bottle. The thermocouple is connected directly to a potentiometer designed for thermocouple use, with high sensitivity but a small range of only 0.02 volt or less. Special potentiometers with a self-contained galvanometer and standard cell are convenient. The dials of the potentiometer are moved at frequent intervals so that the galvanometer reads zero. The readings are recorded every minute or half minute, depending on the rate of cooling; in the immediate neighborhood of a freezing point, they should be taken approximately every quarter minute.

The crystal forms of the various solids frozen out under different conditions are examined with a lens or microscope.

Calculations.—The potentiometer readings for the tin, lead, zinc, and other metals used in calibration are plotted against the time at which the readings were taken. The freezing point of the pure metal corresponds to a flat place on the curve. These temperatures are plotted on a second graph, against the corresponding voltages as read on the potentiometer, and a smooth calibration curve is drawn through the points thus obtained.

Similar voltage-time curves are obtained for the mixtures. There should be two irregularities in each of the curves, except in the cases of the pure metals and the eutectic mixture. The first irregularity corresponds to the freezing out of one component, and the second corresponds to the solidification of the eutectic mixture, *i.e.*, to the appearance of both metals in the solid state.

The thermocouple voltages, corresponding to the flat parts of the curve, are converted into centigrade degrees, with the help of the calibration curve. They represent the freezing points. A third graph is plotted with freezing temperatures against compositions. The intersection of the two parts of the graph gives the eutectic temperature.

Dotted horizontal and vertical lines are drawn through the intersection, and each area, line, and point on the diagram is interpreted in terms of the phase rule.

Practical Applications.—The method of thermal analysis illustrated in this experiment is frequently used in the determination of eutectic points and the formation of compounds. A maximum in the freezing-point-composition curve indicates the existence of an intermediate compound, and the composition of the compound is given by the highest point on the composition-temperature curve, for this represents the melting point of the pure compound.

Temperature-composition curves and other phase-rule diagrams are of great value in the technical study of alloys and in the recovery of a salt by crystallization from a mixture of salts.

Suggestions for Further Work.—Similar measurements may be made with organic compounds, using a test tube and an ordinary 1° thermometer. The following pairs are suitable: urea-phenol, naphthalene-nitrophenol, phenol-p-toluidine.[4,5]

Similar measurements may be made with the system tin-magnesium; this case requires the thermocouple to withstand temperatures up to 800°C. An alumel-chromel couple is satisfactory for this range, but a copper-constantan couple is not satisfactory above 350°. The tin-magnesium system gives a maximum in the freezing-point curve corresponding to $SnMg_2$.

It is a good exercise to prepare definite compounds with the aid of freezing-point curves taken from tables. For example, crystals of sulfuric acid and water, melting at 8.5°C., or crystals of $2NaOH \cdot 7H_2O$ may be prepared. The sulfuric acid–water crystals constitute a menace to partly discharged automobile batteries in cold weather.

The composition of a three-metal alloy which gives the lowest melting point may be determined with the help of a space model in three dimensions. A freezing-point curve showing a eutectic may be determined for bismuth-lead and for bismuth-tin in the same way that the tin-lead curve was determined. The three diagrams are cut out and mounted together vertically so as to form a 60-deg. triangular prism. Three sloping planes are projected along the jagged top of the prism, and the point where the three planes meet gives the lowest freezing point obtainable. The composition of the alloy that has this lowest freezing point is determined by dropping a perpendicular to the basal triangle, and interpreting on the triangular graph shown in Fig. 37. This low-melting alloy is useful in safety plugs and automatic sprinklers.

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37. Three–component Systems

Phase relations in three-components systems are illustrated together with graphing on triangular graph paper.

Theory.—Two-component systems are represented conveniently on rectangular coordinates with percentage composition plotted along one axis and a measured property, such as freezing point, along the other. The percentages of component A and component B always add to 100 per cent.

In three-component systems, the percentages of A, B, and C add up to 100, and it is necessary to use triangular coordinates. An equilateral triangle is used as shown in Fig. 37.

Each of the three apices of the triangle represents one pure component, and the corresponding side is divided into 100 equal parts corresponding to percentages. The composition corresponding to any point within the triangle is readily obtained by counting the percentage toward the apex A, the percentage toward B, and the percentage toward C. These three percentages always add to 100. For example, the point O has the composition 20 per cent A, 30 per cent B, and 50 per cent C. Likewise the point M has the composition 80 per cent A, 10 per cent B, and 10 per cent C. If the figure is turned successively with each apex at the top, the scale of percentage composition is found at the right. The apex represents 100 per cent of the material indicated at the apex.

Various properties may be plotted on a triangular diagram of this type, such, for example, as the appearance of a solid phase at a given

temperature.   The principle is illustrated well by the appearance of two liquid phases in the system ethanol-benzene-water.   Definite mixtures of ethanol and benzene are prepared, and the minimum
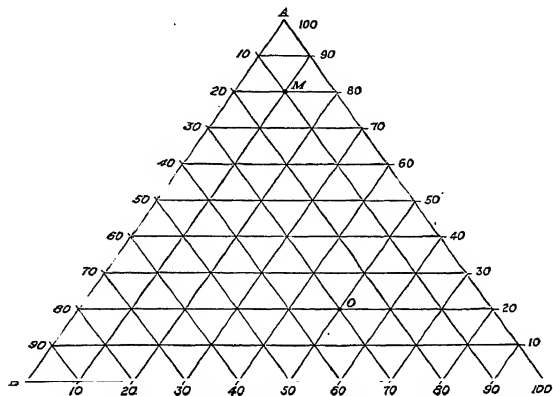
FIG. 37.—Triangular coordinates for three component systems.

quantity of water necessary to give turbidity is determined in each case.

Apparatus.—Thermostat (25°); burette (25 ml); six glass-stoppered bottles (50 ml); ethanol, benzene.

Procedure.—Six different mixtures of ethanol and benzene are made in small glass-stoppered bottles (50 ml) with the following percentages of ethanol: 10, 30, 50, 70, 90, 95.   Twenty grams of each mixture is prepared by running out the proper volumes (accurately) from a small burette.

The bottles containing the different mixtures are set into a thermostat at 25°.   Each in turn is titrated with water to the first appearance of turbidity caused by the presence of a second phase.   During the titration, the bottle is shaken violently after each addition of water. The water is added carefully in small amounts.   It is a good plan to withdraw a small part of the mixture with a pipette before titrating, and after the turbidity is produced the material in the pipette is returned to the bottle.   The turbidity is destroyed by returning this pipetteful of the earlier mixture, and the exact end point is determined again by cautiously adding more water a little at a time.   The titration is expedited in this way because during the first stage large quantities

of water may be added at a time without fear of overstepping the end point.

Calculations.—The percentage of benzene, water, and ethanol is calculated for each of the mixtures that showed turbidity, and these six points are plotted on triangular coordinate paper.

The diagram is discussed in detail, and all the properties of this type of graph are described.

Practical Applications.—The properties of many systems are conveniently described with the help of triangular graphs. The increase in mutual solubility of two liquids, owing to the addition of a third, is of practical as well as theoretical importance.

Suggestions for Further Work.—The tie lines may be drawn in with the help of the distribution ratios of alcohol in water and benzene mixtures as determined from refractive-index measurements and a table.[1]

The same experiment may be carried out at a higher temperature, *e.g.*, 40°. As the temperature is raised, the area under the curve corresponding to the region of two liquid phases becomes smaller, because the liquids become more soluble in each other. Several isothermal lines may be drawn on the same diagram, or a space model may be constructed with temperature as the vertical axis and the triangular diagrams lying in horizontal planes. A triangular-prism space model may be made for the liquid-solid phases in the system diphenyl, diphenylamine, and benzophenone.[6] If time is available, samples of many different compositions are prepared and placed in a thermostat which is raised 1° every half day. The temperature at which each mixture melts is thereby obtained. Wires of different heights representing temperatures are stuck in the triangular base and filled in with plaster of Paris.

Other systems may be measured and plotted.[2,5]

The chloroform, acetic acid, water system[5] is frequently referred to.

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CHAPTER IX

CHEMICAL KINETICS

38. The Hydrolysis of Methyl Acetate

The rate of a chemical reaction is measured and treated mathematically. The specific reaction-rate constant is calculated at two different temperatures, and from these the energy of activation is determined.

Theory.—In predicting the behavior of physical-chemical systems, it is necessary to know the equilibrium conditions, but it is frequently necessary to know, also, the speed with which the equilibrium is attained. In most of the reactions of inorganic chemistry, equilibrium is attained in so short a period of time that the reaction appears to be instantaneous, but in many of the reactions of organic chemistry, the time variable is extremely important. Often it is more important than the equilibrium.

The fundamental law underlying all reaction rates is the mass law, or concentration law. According to this law, the rate of the chemical reaction depends on the effective concentration of the reacting materials. If only one molecule is involved, the reaction is called unimolecular. If two molecules react together, the reaction is bimolecular. Termolecular reactions and reactions of higher orders are rare.

Many reactions follow the first-order equation

$$dc \qquad (1)$$

which expresses mathematically the fact that the rate of decrease of concentration c with time t is proportional to the concentration. Integrating this equation,

$$-2.303 \log c = kt + C \qquad (2)$$

Integrating between limits c_1 at t_1 and c_2 at a later time t_2,

$$k \qquad \frac{2.303}{t_2 - t_1} \log \frac{c_1}{c_2}$$

Also

$$\frac{2.303}{t} \log \frac{c_0}{c} \tag{4}$$

where c_0 represents the concentration at the beginning of the experiment and c the concentration after time t.

The constant k is called the "reaction-velocity constant" or, better, the "specific reaction rate." It is a number that expresses the fraction of the material that reacts in a unit of time. It may be expressed in reciprocal seconds or minutes.

Many reactions follow the first-order equation, when in reality there are two molecules involved in the reaction. If, in a bimolecular reaction, one reacting material is greatly in excess, its concentration does not appear to change; then the first-order equation applies. Sometimes a trace of catalyst is present, and its concentration does not change, although it takes part in the reaction.

Frequently there are complications of two or more reactions going on simultaneously. In some cases, near the end of the reaction, the reverse reaction must be considered.

The course of a reaction must be followed in such a way that the concentrations of the reacting materials are not disturbed. The best way is to determine the concentration of reacting material by measuring some physical property, such as volume, electrical conductance, optical rotation, or the quantity of gas evolved. If it is necessary to resort to chemical analyses, samples are drawn off and titrated. The reaction taking place in the sample may be stopped, if necessary, by cooling or by the addition of a suitable reagent.

Methyl acetate hydrolyzes in water to give methanol and acetic acid, according to the reaction

$$CH_3COOCH_3 + H_2O \qquad \cdot CH_3COOH + CH_3OH + H^+$$

The reaction is catalyzed by hydrogen ions and, in fact, it does not proceed with measurable velocity in pure, neutral water. Although two molecules are involved in this reaction, the water is in such large excess that only the methyl acetate appears to change in concentration. The large excess of water prevents the reverse reaction.

A determination of the specific-rate constant at two or more temperatures permits a determination of the activation energy E defined by equation (5) where T refers to absolute temperature

$$\frac{d \ln k}{dt} \qquad \frac{E}{RT^2} \tag{5}$$

or in integrated form by equation (6)

$$\log \frac{k_2}{k_1} = \frac{}{2.303RT_2} \tag{6}$$

This energy E, usually expressed in calories per mole, is the extra energy that must be supplied in order to put the molecules in an activated condition so that they undergo chemical change.

Apparatus.—Thermostats at 35° and at 25°; four 150-ml Erlenmeyer flasks; 5-ml pipette; watch or electric clock; methyl acetate; 2 liters 0.2N sodium hydroxide; 500 ml 2N hydrochloric acid; 1 liter distilled water free from carbon dioxide.

Procedure.—The concentration of methyl acetate, at any time, is determined by titration of samples with 0.2N sodium hydroxide.

The success of the experiment depends chiefly on the care used in pipetting and titrating. The hydroxide and the solutions must be quite free from carbonates, otherwise a fading end point is obtained with phenolphthalein. The sodium hydroxide solution is made by diluting a few milliliters of a saturated solution of sodium hydroxide. Sodium carbonate is less soluble than sodium hydroxide, and in a saturated solution of hydroxide the carbonate is thrown out.

The distilled water used in making the solutions is freed from carbon dioxide by placing in a liter flask and bubbling through air that has passed through a tower of soda lime or askarite. Ten minutes of active bubbling should be sufficient. The carbon dioxide may be removed also by vigorous boiling followed by cooling in a stoppered flask. The Erlenmeyer flasks used in the experiment are thoroughly cleaned, rinsed, and dried.

Since the sodium hydroxide solution can be used for other experiments, it is a good plan to make up 2 liters. It is standardized against a standard acid solution and kept away from air.

Fifty milliliters of exactly 2N hydrochloric acid is placed in a 150-ml flask with 45 ml of water, free from carbon dioxide, and stoppered. Another solution is placed in a second flask for a check determination. The two flasks are clamped in a thermostat at 35° and allowed to stand for 10 or 15 min. Some methyl acetate in a test tube is also set into the thermostat.

When the solutions have come to the temperature of the thermostat, exactly 5 ml of the methyl acetate is pipetted into one of the flasks. It is shaken to mix thoroughly, and a sample of exactly 5 ml is withdrawn immediately and run out from a pipette into 50 ml of water, free from carbon dioxide, in a flask. The dilution with water

arrests the reaction somewhat, but the solution should be titrated at once. The error can be further minimized by chilling the water in an ice bath. The time at which the pipette starts to drain into the water of the titration flask is recorded accurately together with the titration.

Two more samples are titrated in a similar manner after 5-min. intervals, two additional samples are taken at 10-min. intervals, and then a few at 20-min. intervals. About half an hour after starting the first reaction the check determination is started, and the two are carried along together. The remaining solutions (at least 25 ml in volume) are stoppered and allowed to stand in the desk for a couple of days in order to permit a final titration when the reaction is completed.

Additional determinations are carried out at 25° in the manner just described for 35°. The reaction goes less than half as fast, and samples are taken at 15-min. intervals for an hour and then at 30-min. intervals for 2 or 3 hr. more. The second determination may be started shortly after the first one as titrations are not required so frequently. Again a sample of the remaining solutions is retained for a final titration after standing at least 2 days.

Calculations.—The difference between the titration at any time t and the titration at the end of 2 days, when the reaction is completed, is a measure of the concentration of methyl acetate remaining unhydrolyzed at time t. Each molecule of methyl acetate that hydrolyzes produces one molecule of acetic acid, and the increase in acidity is a direct measure of the amount of methyl acetate that has reacted. The amount of hydrochloric acid remains unchanged throughout the experiment.

The concentrations of methyl acetate calculated from the differences between the titration values and the final titration are arranged in tabular form. They are plotted against time, and as time is the independent variable it is plotted along the X-axis. One set of determinations is represented by circles and the other by crosses. A smooth curve is drawn through the points.

A second graph is drawn, in which log c is plotted against time for both determinations, and the best straight line is drawn through these points. Two lines are graphed, one for 25° and one for 35°. The specific reaction rates k are calculated from the slopes of the lines, using equation (2).

A table is prepared; the values of k over the different time intervals are calculated by equation (3). These are compared in a general way with the values of k determined graphically, but it is not significant[7] to average the constants obtained by equation (3). The activation

energy E is calculated from the values of k at the two temperatures, using equation (6).

Practical Applications.—The speed of a chemical reaction is important in determining the efficiency of many industrial chemical reactions. In organic reactions particularly, where there is the possibility of several reactions going on simultaneously, that reaction which is fastest is the one that predominates. The present experiment illustrates the simplest mathematical expression for the rate of a chemical reaction.

The rate of hydrolysis of methyl acetate is useful in calculating the concentration of hydrogen ions in a solution.

Suggestions for Further Work.—The reaction rates may be determined at other temperatures, and the energy of activation checked by determinations over other temperature intervals.

Other acids may be used, and the influence of neutral salts, hydroxyl ions, or organic materials may be studied. Methyl acetate may be replaced by other esters, higher temperatures being used if necessary.

The extent of hydrolysis of a salt may be determined by measuring the rate at which methyl acetate is hydrolyzed when added to the salt solution.

Instead of estimating by eye the best straight line passing through the log c vs. time graph, the equation for the line may be determined by the method of least squares.

Other statistical methods may be used in the closer estimation of k.[7]

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39. The Inversion of Cane Sugar

This experiment illustrates the use of the polarimeter, the calculation of reaction-rate constants, and the influence of substitution of atoms on the ionization of an organic acid.

Theory.—The theory is discussed in Exp. 38.

The inversion of cane sugar is an excellent reaction to study, because it can be followed without disturbing the system. The angle of rotation of polarized light passing through the solution is measured with a polarimeter. The reaction is

$$C_{12}H_{22}O_{11} + H_2O + H^+ \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6 + H^+$$
$$\text{(Sucrose)} \qquad\qquad \text{(Glucose)} \quad \text{(Fructose)}$$

The sucrose is dextrorotatory, and the resulting mixture of glucose and fructose is slightly levorotatory because the levorotatory fructose

is slightly more active optically than the dextrarotatory glucose. As the sucrose is used up and the inverted sugar is formed, the angle of rotation to the right becomes less and less and finally the light is rotated to the left. The rotation is determined at the beginning and at the end of the reaction, and the algebraic difference between these two readings is a measure of the original concentration of the sucrose. At any time t, a number proportional to the concentration c of sucrose is obtained from the algebraic difference between the final reading and the reading at the time t.

The reaction proceeds too slowly to be measured in pure water, but it is catalyzed by hydrogen ions. The water is in such large excess that the reaction follows the equation for a first-order reaction, although it is a bimolecular reaction.

Apparatus.—Polarimeter (described on page 52); mercury-vapor lamp with filters (page 395) or sodium-vapor lamp; thermostat and circulating pump; two water-jacketed polarimeter tubes; pure sugar; 100 ml of $4N$ trichloroacetic acid; 100 ml of $4N$ monochloroacetic acid. (**Caution.**—The trichloroacetic acid is corrosive.)

Procedure.—Twenty grams of pure cane sugar (rock candy) is dissolved in water (filtered, if necessary, to give a clear solution) and diluted to 100 ml.

Two jacketed polarimeter tubes are connected in series with the circulating water from a thermostat at 25°, and set in the polarimeter. A zero reading is taken with a mercury-vapor lamp and Corning glass filters arranged to transmit only the green light (page 395). A sodium-vapor lamp is equally satisfactory. A small crystal of rock salt, placed on a Méker burner, may be used in case special lamps are not available.

After letting the sugar solution and a solution of exactly $4N$ trichloroacetic acid solution stand in the thermostat for a few minutes, 25 ml of each are mixed thoroughly. One of the polarimeter tubes is rinsed out with successive small portions of the solution, and then the tube is filled with the solution and stoppered. The second tube is filled, in a similar manner, with a mixture of the sugar solution and exactly $4N$ monochloroacetic acid solution (exactly 25 ml of each). The tubes are filled as soon as possible after mixing, so that an early reading of the angle of rotation may be obtained.

The time of the first reading is recorded, and polarimeter readings of the trichloroacetic acid and the corresponding times are taken as rapidly as convenient (10 min.) over a period of 1 hr. or so. As the reaction slows down, the observations may be taken less frequently. The observations should extend over a period of 3 hr. or more. The

reaction goes much more slowly with the monochloroacetic acid, and the readings are taken less frequently. They are taken when convenient between readings on the trichloroacetic acid.

The final readings are taken after the solutions have stood for at least 2 days in a tightly stoppered flask in the case of the trichloroacetic acid and a week in the case of the monochloroacetic acid, and the reaction has been completed. It is important to preserve a sufficient quantity of each of the original solutions to rinse and fill the polarimeter tube for these readings.

Calculations.—The time is plotted along the X-axis, on coordinate paper, and the corresponding concentrations along the Y-axis. The change in rotation is a measure of the extent of the reaction, and the rate of reaction decreases with time in accordance with the mass law.

As stated before, the concentration c of sucrose may be expressed in terms of the angles of rotation and is proportional to $\alpha - \alpha_\infty$ where α is the angle of rotation at time t and α_∞ is the final angle (negative in this particular case). The logarithms of the concentrations of sucrose are plotted against time. The best straight line is drawn through the points, one for the trichloroacetic acid and one for the monochloroacetic. The specific reaction rates are calculated from the slope of the lines.

The ratio of the constants for the two different acids is a measure of the ratio of activity of the hydrogen ions of the acids at $2N$, provided that in both cases the acids were exactly $4N$. This ratio may be compared with the hydrogen ion concentration ratio calculated from dissociation constant and concentration data.

A calculation is made to show what the concentration of sucrose was in each case exactly 10 hr. after starting the reaction, and the precision with which this prediction can be made.

On the assumption that the trichloroacetic acid is completely dissociated, and that the rate of inversion is directly proportional to the effective concentration of hydrogen ions, the degree of ionization of monochloroacetic acid in $2N$ solution and the ionization constant (page 176) are calculated. The rate of this reaction depends on the concentration of the sucrose and water, but these quantities appear to remain constant when the reaction is carried out as described.

Practical Applications.—These are discussed under Exp. 38.

Suggestions for Further Work.—These are discussed under Exp. 38.

Duplicate determinations may be made on a second day to ascertain how closely they agree.

Hydrochloric acid and sulfuric acid, each $2N$, may be used in place of the $4N$ chloroacetic acids.

The activation energies may be calculated by running a second set of determinations, using water pumped from a thermostat at 20°.

A mixture of methyl acetate and sucrose may be followed with both titration and rotation measurements, to determine if the hydrogen ions can catalyze both reactions simultaneously with undiminished efficiency.

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40. The Hydrolysis of Acetal

The use of the dilatometer in following the rate of a reaction is illustrated with a reaction catalyzed by hydrogen ions. The data are used to calculate the degree of dissociation of a weak acid.

Theory.—When the products of a reaction occupy a larger (or smaller) volume than the reactants, the progress of the reaction can be followed with a dilatometer. The solutions should be dilute so that the change in volume is directly proportional to the extent of the reaction, uncomplicated by changing concentrations. The dilatometer should have a large bulb and fine capillary, so as to be sufficiently sensitive, but it should be no more sensitive than is justified by the temperature control of the thermostat. Very small capillaries are inconvenient to use.

The hydrolysis of acetal, catalyzed by hydrogen ions, to give acetaldehyde and ethanol, is a reaction suitable for dilatometric measurement. The reaction is

$$CH_3CH(OC_2H_5)_2 + H_2O + H^+ \rightarrow CH_3CHO + 2C_2H_5OH + H^+$$
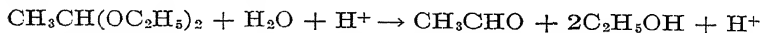
The water is in large excess and the concentration of the catalyst remains unchanged, so that the rate of the reaction is directly proportional to the concentration of the acetal. The reaction, then, follows the first-order equation.

The specific reaction rate of this reaction and other reactions of a similar nature may be used to determine the effective concentration of hydrogen ions.

Apparatus.—Dilatometer; thermostat regulated at 25° to 0.01 or 0.02°; acetal.

Procedure.—The dilatometer is shown in Fig. 38. A capillary tube with 1-mm bore is fused to a U tube slightly less than 50 ml in volume provided with a selected, tightly fitting stopcock* and a narrow filling

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* Stopcocks on pieces of apparatus of this sort should be of the interchangeable kind.

tube. A narrow millimeter scale at least 10 cm long is attached to the tube.

An aqueous solution of freshly distilled acetal, approximately 0.4M, is placed in a flask in the thermostat, and allowed to come to temperature. A 0.001M solution of hydrochloric acid is also placed in the thermostat. The empty dilatometer is mounted vertically in the thermostat with the capillary extending above the water in a convenient position for reading the scale. After waiting a few minutes for attainment of the thermostat temperature, 25 ml of each solution is measured out with a pipette, and the two are mixed thoroughly. The concentration of hydrochloric acid will then be 0.0005M, and the acetal approximately 0.2M. The mixture is poured at once into the filling bulb of the dilatometer. The dilatometer is filled quickly. It should not be held in the hands on account of thermal affects. When the level of the liquid reaches the lower part of the scale, the stopcock is firmly and tightly closed. The stopcock must be maneuvered so that no air bubbles are present.

The level of the liquid shown on the scale is recorded every 3 or 6 min. at first, and then at less frequent intervals as the reaction slows down. The exact time at which each observation is made is recorded. The observations are continued until there is no further change in the volume of the solution. Check determinations should be made as usual. If two dilatometers are available, a second experiment may be started after the first one has slowed down sufficiently to permit the observer to divide his attention.

If there is a chance that the thermostat is not regulating to 0.02°, it is a good plan to have an extra dilatometer, of the *same dimensions* as the first, filled with water and set close by the first thermostat. Its scale readings are recorded at the same time as those of the first dilatometer, and if any changes are observed they constitute corrections which are subtracted from the readings of the first dilatometer.
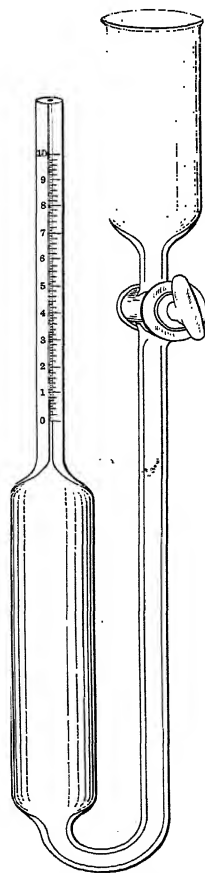

FIG. 38.—Dilatometer for liquids.

A second experiment is carried out, using $0.1M$ acetic acid instead of the $0.001M$ hydrochloric acid.

In a third experiment (if time permits) a mixture of acetic acid and sodium acetate is used which is $0.1M$ with respect to acetic acid and $0.002M$ with respect to sodium acetate.

Calculations.—The concentration c of acetal at the beginning of the observations is measured by the total increase in volume during the course of the whole reaction. Since the reaction is of the first order, it is not necessary to specify the concentration in absolute units, and so they are designated only in terms of scale divisions. The concentration, at any time t, is proportional to the difference between the reading r_t at that time and the final reading r_∞ when the reaction is completed and no further change occurs. Then $\log (r_\infty - r_t)$ is plotted against the time, and the best straight line is drawn through the points. The first few points may be neglected if the mixture has not reached the temperature of the thermostat. The mixing process produces a slight thermal change. The negative of the slope of the line multiplied by 2.303 gives the specific reaction rate for the reaction as explained in Exp. 38.

On the assumption that the specific reaction rate is directly proportional to the hydrogen-ion concentration and that the dilute hydrochloric acid is completely dissociated, the concentration of hydrogen ions and the degree of dissociation of the acetic acid may be calculated.

In like manner, the degree of dissociation of the acetic acid in the presence of sodium acetate may be calculated.

Practical Applications.—The dilatometer may be used in the study of the rates of various reactions occurring in the liquid state. The method described here is useful for determining the effective concentration of hydrogen ions. It has been found valuable for determining the strength of acids and bases in nonaqueous solvents.[4]

Suggestions for Further Work.—The assumption that the specific reaction rate is directly proportional to the hydrogen-ion concentration may be verified by using three or four concentrations of hydrochloric acid, ranging, after mixing with acetal, from 0.001 to $0.0003M$.

The strength of other acids, such as monochloroacetic, trichloroacetic, sulfuric, and boric, may be determined in the manner described for acetic acid.

The concentration of hydrochloric acid may be so adjusted that the reaction rate can be measured conveniently at several temperatures (*e.g.*, 0°, 20°, 30°), and from these data the energy of activation may be calculated.

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41. The Saponification of Ethyl Acetate.   A Bimolecular Reaction

This experiment illustrates a bimolecular reaction for which a second-order constant may be calculated.   The accuracy of the results is a good test of the experimenter's skill in titration and analytical technique.

Theory.—The rate constant k for chemical reactions is given by the following equation:

$$k = se^{\overline{RT}}$$

where e = the base of the natural logarithms.

E = the energy per mole required for activation.

R = the gas constant.

T = the absolute temperature.

The expression $e^{\frac{-E}{RT}}$ represents the fraction of molecules having an energy equal to or greater than the energy required for activation.   For bimolecular gas reactions, the constant s is probably about equal to the number of molecules colliding.   Reactions in solution have not been worked out so completely as yet.

The rate of a second-order reaction dx/dt is proportional to the concentration of each of the two reacting materials, as expressed in the equation
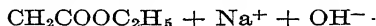
$$\frac{dx}{dt} = k(a - x)(b - x)$$

where x = the number of moles reacting in time t.

a = the initial concentration of one reacting material.

b = the initial concentration of the other.

k = the specific reaction rate.

The bimolecular reaction studied in this experiment is the saponification of an ester by sodium hydroxide.

$$CH_2COOC_2H_5 + Na^+ + OH^- \cdot \qquad\qquad Na^+ + C_2H_5OH$$

The hydroxyl ion and ethyl acetate are the reacting materials, the sodium ion being incidental.

Apparatus.—Thermostat; two Erlenmeyer flasks (1,000 ml); 250-ml flask; 50-ml pipette; 0.01M ethyl acetate, 0.02M sodium hydroxide, 0.02M hydrochloric acid.

Procedure.—Distilled and neutral ethyl acetate is dissolved in water to give about 500 ml of 0.01M solution.   Two liters of 0.02M

sodium hydroxide is prepared, free from carbonates (page 446).   The distilled water from which these solutions are made is treated to remove the dissolved carbon dioxide, because the success of the experiment depends on the accuracy of titration, and the end point is not sharp if carbon dioxide is present.   A stream of air is passed through a tower of soda lime and bubbled through the water in a vigorous stream for 10 or 15 min.   Exactly 250 ml of each solution is placed in Erlenmeyer flasks, which have been cleaned, steamed, and dried, and they are set into a thermostat at 25° for about 15 min., or until they have acquired the temperature of the thermostat.

The reaction is started by pouring the ethyl acetate solution rapidly into the sodium hydroxide solution and shaking thoroughly. The time of mixing is recorded.

Fifty-milliliter samples are withdrawn and titrated after about 2, 5, and 8 min.   The time of discharge of the pipette is noted accurately, and the sample is discharged as rapidly as possible into a known excess of $0.02M$ hydrochloric acid.   A free-flowing pipette should be used. The solution is then titrated with $0.02M$ sodium hydroxide, using phenolphthalein as an indicator.   Further samples are titrated after longer intervals of time as the reaction slows down.   The last 100 ml or more is stoppered and allowed to stand for a day or two to give the final titration value after the reaction has gone to completion.

A second experiment is started about half an hour later, when the first reaction has slowed down somewhat.   If the first titrations cannot be made fast enough to permit proper sampling, the samples may be kept in stoppered bottles after acidifying.

The experiment is repeated under the same conditions except with the ethyl acetate half as concentrated.

Calculations.—The concentration a of sodium hydroxide, in moles per liter at the beginning of the experiment, is calculated from the original solutions and the volume of the mixture.   All concentrations are expressed in moles per liter.

As the reaction proceeds, each hydroxyl ion removed in the formation of the nontitratable alcohol removes one molecule of ethyl acetate, and the number of moles of either hydroxyl ion or ethyl acetate removed per liter in this way is designated as x.

The value of x, at any time t, is determined by subtracting the concentration of sodium hydroxide at time t from the original concentration a.   This concentration is obtained by back titration with the sodium hydroxide after adding the excess of hydrochloric acid.

The number of moles b of ethyl acetate originally present is determined by subtracting the final concentration of sodium hydroxide from

the original concentration a. The final concentration is obtained by titrating after a day or more when all the ethyl acetate has reacted. The final titration gives the excess of sodium hydroxide over ethyl acetate in the original solution. The experiment is arranged so that there is an excess of sodium hydroxide to permit this calculation.

The integrated expression for a second-order reaction is

$$k = \frac{2.303}{t(a - b)} \log \frac{b(a - x)}{a(b - x)}$$

and, as explained above,

$t =$ time from start of reaction.

$x =$ moles of sodium hydroxide or ester in a liter of solution which react in time t.

$a =$ moles of sodium hydroxide originally present in a liter.

$(a - x) =$ moles of sodium hydroxide per liter present at time t.

$b =$ moles of ester per liter originally present.

$(b - x) =$ moles of ester per liter present at time t.

When the initial concentrations a and b are equal, the equation is simpler, as follows,

$$\cdots\ \cdots\ ta\ (a - x)$$

When there is only a very slight excess of sodium hydroxide, this formula gives better results than the first one.

The value of the specific reaction rate k is determined by finding the slope of the best straight line passing through the points obtained by plotting $\log b(a - x)/a(b - x)$ against the time and multiplying the slope by $2.303/(a - b)$. It is checked with individual values, calculated directly from the original data, using the integrated formula.

If titrations in milliliters are used in the calculations, a constant will be obtained, but it will have different numerical values, depending on the concentration of the titrating solution. The concentrations should be expressed always in moles per liter in order to make possible comparison with other values recorded in the literature.

Practical Applications.—The calculation of this experiment is typical for any second-order reaction, and the influence of concentration of either reacting material on the velocity of the reaction may be calculated quantitatively.

Suggestions for Further Work.—The experiment may be repeated at 20 and 30° in order to determine the temperature coefficient of the reaction and the energy of activation.

The rate of saponification of other esters may be determined. Methyl acetate saponifies rapidly, and it should be studied at lower temperatures. The more complicated esters saponify more slowly, and they may be studied conveniently at

higher temperatures. The saponification rate is the same with all strong bases, but with weak bases the reaction is complicated and depends on the degree of dissociation of the base.

The reaction may be followed by measuring the change in the electrical conductance of the system[3] starting with equal concentration of alkali and ester. A decrease in conductance is caused by replacing the mobile hydroxyl ion with the slow acetate ion, and the amount of the decrease is proportional to the fraction of the ester which has reacted. The final conductance is determined at the same temperature after the mixture has stood for at least a day. The initial conductance is determined by mixing the sodium hydroxide with an equal volume of water instead of ethyl acetate solution because the reaction with ethyl acetate goes so fast as to prevent an initial measurement.

The number of moles x that have reacted at time t is proportional to the total decrease in conductance up to the time t, and the original concentration of both ester and hydroxyl ions is proportional to the difference between the initial and final conductance. The fraction of ester (and hydroxyl ion) remaining at time t is obtained by dividing the decrease in conductance at time t by the total decrease when the reaction is completed.

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42. Clock Reactions

Clock reactions are reactions that go on for a time unobserved and then suddenly give a color change or precipitate indicating that the reaction has been completed. This reaction makes a good lecture demonstration, and it is used here to illustrate the formulas of chemical kinetics which deal with the influence of concentration on reaction rate.

Theory.—Sometimes a slow reaction is followed immediately by a rapid reaction under conditions such that the second reaction does not start until the first one is completed. In the following reactions, a blue color is produced with surprising suddenness after a preliminary period the length of which depends on the concentration of the solution.

The first slow reaction is

$$3H_2SO_3 + HIO_3 \rightarrow 3H_2SO_4 + HI$$
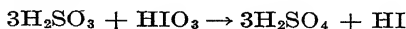
The sulfurous acid is produced by mixing sodium sulfite and sulfuric acid; the iodic acid is formed in a similar manner from potassium iodate.

When all the sulfurous acid has been oxidized, the following reaction occurs very rapidly:

$$5HI + HIO_3 \rightarrow 3I_2 + 3H_2O$$
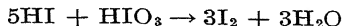
The iodine produced in this reaction turns starch blue, but as long as sulfurous acid is present, any iodine will be reduced back to hydriodic acid.

Apparatus.—Stop watch, or electric clock; 500-ml flasks; two 25-ml pipettes; one 100-ml graduated cylinder; 2 liters $0.02M$ iodate; 1 liter $0.01M$ sodium sulfite which is also $0.04M$ in sulfuric acid; starch.

Procedure.—To something less than a liter of $0.04M$ sulfuric acid is added a paste made by mixing 1.26 g of sodium sulfite and 5 g of starch (preferably "soluble" starch) with a few milliliters of water. The solution is then thoroughly mixed and diluted to 1 liter. Two liters of $0.02M$ potassium iodate is prepared.

The iodate and the sulfite solutions are mixed in varying proportions, and the time from mixing to the appearance of the blue color is determined accurately with a stop watch or an electric clock. The order of the reaction and the specific reaction rate k is estimated from a knowledge of the concentrations in the reaction mixtures and the time required for the appearance of the blue color. The solutions, in proper amounts, are placed in open beakers, and the iodate solution is added quickly to the sulfite solution as the stop watch is started. The volume of the final reaction mixture must be kept constant, and the calculated amount of distilled water is added to the sulfite solution so that when the iodate solution is poured in the total volume will be 200 ml. The temperature must be constant within a degree at 25° or at room temperature. If the end point is not sharp, more starch is added.

The schedule in the following table is suitable for showing the influence of concentration on reaction rate.

MILLILITERS OF REACTING SOLUTIONS AND WATER TO GIVE A FINAL VOLUME OF 200 ML

Na_2SO_3	H_2O	KIO_3	Na_2SO_3	H_2O	KIO_3
75	50	75	50	0	150
50	75	75	25	25	150
25	100	75	20	30	150
15	110	75	15	35	150
10	115	75	10	40	150
5	120	75	5	45	150

If time permits, some of the determinations are repeated at a low temperature in an ice bath.

Calculations.—It is desired to estimate the order of the reaction with respect to each of the reagents and to evaluate the specific rate constant. The concentration in moles per liter is calculated for the sulfite and the iodate in the final volume of 200 ml. The time of reaction is plotted against the reciprocal of the sulfite concentration, holding the iodate concentration constant at 0.0075 moles per liter ($\frac{75}{200} \times 0.02$) and the best straight line is drawn through the points. A similar plot is made for the reciprocals of the concentrations of sulfite, with the iodate concentration constant at 0.0150 moles per liter, and the slopes of the two lines are compared.

It is instructive also to plot the time of reaction against the concentration and then against the log of the concentration and the reciprocal of the concentration for each reactant, holding the other reactants constant.

Suggestions for Further Work.—A similar reaction[3] involving arsenite instead of sulfite may be studied.

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43. Catalysis.   The Decomposition of Hydrogen Peroxide

The behavior of catalysts and promoters is studied as they affect the decomposition of hydrogen peroxide. The reaction is followed by measuring the evolution of gas, and first-order constants are calculated.

Theory.—Many substances increase the velocity of chemical reactions, and are found in their original concentration at the end of the reaction. These substances are called "catalysts." Although they do not appear in the stoichiometric equations for the reaction, they often do have a part in intermediate reactions. For convenience, catalysis is divided into heterogeneous catalysis involving surfaces and into homogeneous catalysis.

Promoters are substances that increase the catalytic effect. They are, in fact, catalysts for the catalyst. Inhibitors or poisons, on the other hand, decrease the catalytic effect.

The decomposition of hydrogen peroxide is easily followed, and it is particularly well adapted for study because it responds to many different catalysts. Even the slow decomposition is probably catalyzed.[1]

Apparatus.—Thermostat; 50-ml flask; gas burette; 10-ml pipette; 3 per cent (approximate) pure hydrogen peroxide, potassium iodide, ferric chloride, cupric chloride.

Procedure.—A 50-ml round-bottomed flask with a rubber stopper is connected with a short length of thick-walled rubber tubing to a gas burette and set into a thermostat at 25° where it is shaken violently by hand while immersed in the thermostat bath. A 5-ml pipette full of 3 per cent hydrogen peroxide is drained into the flask, and two or three pieces of fire-polished glass rod are added in order to increase the agitation of the liquid. The stopper is inserted tightly, the gas burette is adjusted, and the flask is shaken for several minutes. In the absence of a catalyst, no appreciable oxygen should be evolved. Some commercial grades of hydrogen peroxide are not suitable for this experiment for they contain added inhibitors such as acetanilide. The concentrated chemical "peroxydol" is satisfactory after dilution.

The flask is removed from the thermostat, 10 ml of the catalyst is added from a pipette, and the stopper is immediately replaced. The flask is returned to the thermostat and shaken vigorously and continuously with a pendulum motion. After a few minutes, equilibrium conditions of temperature and saturation are reached, and the volume of the gas is recorded at frequent intervals until the decomposition is complete and the evolution of gas ceases, ordinarily in the course of 15 to 30 min. If the final volume is not close to the capacity of the burette, the quantity of peroxide is changed. It is important to obtain the final volume, and if the decomposition proceeds too slowly for convenience, the final reading may be obtained by heating the solution to about 50° for a few minutes and returning the flask to the thermostat.

Several different catalysts may be added with a 10-ml pipette in approximately the following concentrations:

1. Potassium iodide solution, $0.2M$.
2. Potassium iodide solution $0.05M$.
3. Ferric chloride solution,[2] $0.1M$ with respect to ferric chloride and $0.5M$ with respect to hydrochloric acid.
4. Ferric chloride plus cupric chloride[2] (solution 3, to which has been added sufficient solid cupric chloride to give $0.1M$ cupric chloride).
5. Cupric chloride solution,[2] $0.1M$ with respect to cupric chloride and $0.5M$ with respect to hydrochloric acid.

The potassium iodide involves an alternate oxidation and reduction process which leads to a rapid decomposition. The ferric chloride probably forms an intermediate compound ferric acid, with the hydrogen peroxide, which then decomposes rapidly. The cupric

chloride is not effective itself, but it acts as a promoter for the ferric chloride.[3]

Calculations.—The concentration c of undecomposed hydrogen peroxide remaining at any time t is proportional to $v_\infty - v_t$ where v_∞ is the final volume of oxygen evolved and v_t is the volume at time t. The specific reaction rate k is obtained by plotting log c against t. (Exp. 38).

Hypotheses are offered to explain the behavior of the various added reagents.

Practical Applications.—The student is referred to special texts for the many applications of catalysis in industrial and synthetic chemistry. The production of ammonia from nitrogen and hydrogen by the Haber process is an outstanding example, as is also the synthesis of methanol from carbon monoxide and hydrogen, using zinc oxide as a catalyst.

Acetanilide is used commercially as an inhibitor for keeping hydrogen peroxide.

A study of catalysts for the decomposition of hydrogen peroxide is valuable in connection with the study of enzymes and certain physiological processes. The promotion of the catalytic effect of ferric salts by copper salts is important in biological chemistry, for traces of copper salts with iron salts have been found effective in the cure of anemia.[4]

Suggestions for Further Work.—Other substances may be examined for catalytic properties, including colloidal platinum and colloidal platinum poisoned with a trace of mercuric chloride.[5] The enzyme catalase is another interesting catalyst for this reaction.

Some of the rate measurements may be carried out at other temperatures, log k is plotted against $1/T$, and from the slope of the line the energy of activation is calculated.

The influence of concentration of the catalyst ferric chloride and the promoter cupric chloride may be studied.

A solution of bromine, potassium bromide, and sulfuric acid acts as a catalyzer.[6] It is an interesting example of a "steady" state in which an intermediate substance is produced by one reaction and decomposed by another, giving rise to a definite concentration which is maintained during a considerable part of the reaction.

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CHAPTER X

ELECTRICAL CONDUCTANCE

44. Conductance Behavior of Weak and Strong Electrolytes

In this experiment, practice is obtained in determining the electrical conductance of solutions. The influence of concentration on the conductance of strong and weak electrolytes is studied, and the dissociation constant of a weak acid is determined.

Theory.—In general, the pure solvents are poor conductors of electricity, but when acids, bases, or salts are dissolved in them, conductance is increased, sometimes to a very large extent.

The conductance of these solutions is the result of the actual movement of ions through the solution to the electrodes. When two electrodes of an electrical circuit are placed in a solution, the cations $(+)$ are attracted to the negative pole (cathode) and the anions $(-)$ are attracted to the positive pole (anode). Changes in the conductance of an electrolyte solution due to variations in concentration may result from changes both in the number and in the mobility of the ions present.

Strong electrolytes are those like sodium chloride which are largely dissociated into electrically charged ions even in fairly concentrated solutions, and weak electrolytes are those like acetic acid which are only slightly dissociated into ions even in dilute solutions.

The difference in behavior between a weak and a strong electrolyte becomes evident when the equivalent conductance of their solutions is plotted as some function of the concentration, especially in the dilute regions. The equivalent conductance for the strong electrolyte approaches a definite value at infinite dilution, but that of the weak electrolyte, though also increasing with dilution, cannot be extrapolated to a definite value. When the electrolyte is weak, the increase in conductance is due largely to an increase in the number of ion carriers, corresponding to a higher degree of dissociation as the solution is diluted. This is the basis of the theory of Arrhenius, proposed in 1887, which has been so successful in describing quantitatively the behavior of weak electrolytes. The increase of equivalent conductances of solutions of strong electrolytes with dilution is due not to an increase in dissociation, because the dissociation is already nearly complete, but

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to an increased mobility of the ions. In a concentrated solution of a highly ionized strong electrolyte, the ions are quite close to one another, so that any one of them in moving is influenced not only by the electrical field due to the voltage impressed on the electrodes, but also by the field of the surrounding ions. The ionic velocities are dependent upon both forces. Arrhenius attempted to treat the electrolytic conductance behavior of the strong electrolytes in the way that he had successfully treated the weak electrolytes; but such a treatment is inconsistent with the fact discovered by Kohlrausch that the equivalent conductance plotted against the square root of the concentration gives a line for strong electrolytes which is nearly straight. More recently Debye and Hückel, and Onsager have been able to calculate the effect of the surrounding ions on the mobility of any given ion and have obtained a result entirely consistent with the experimental facts. Complete dissociation is here assumed.

A great deal more study has been devoted to the conductance behavior of aqueous solutions than of nonaqueous solutions, but the newer theories as expounded by Debye, Onsager, Kraus, Fuoss, and others are being applied to the nonaqueous solutions. And the nonaqueous solutions are now receiving more attention than previously. The dissociation constant K for the weak electrolyte may be calculated from the degree of ionization and the concentration, using the formula

$$\frac{\alpha^2 c}{1 - \alpha} = K_D \tag{1}$$

where α is the degree of dissociation and c is the concentration in moles per liter. It has no significance when applied to strong electrolytes where α is practically unity.

The data for a strong electrolyte may be represented conveniently in graphical form, in which the equivalent conductances are plotted against the square root of the concentration. For a uniunivalent electrolyte[5] the limiting slope of the curve obtained in this way should obey the equation

$$\Lambda = \Lambda_0 - (a\Lambda_0 + b)\sqrt{c} = \Lambda_0 - A\sqrt{c}$$

where $a = 0.2274$ and $b = 59.79$ in water at 25°. For potassium chloride, $\Lambda_0 = 149.8$; thus $\Lambda = 149.8 - 93.85\sqrt{c}$ at 25°.

Apparatus.—Wheatstone bridge; conductance cell; source of alternating current; key; telephone receiver; conductance water; platinizing solution; *exactly* 0.02N potassium chloride solution; *exactly* 0.05N solution of acetic acid; thermostat at 25°C.

Procedure.—The apparatus is shown in Fig. 39, and more details of the electrical apparatus may be found on pages 364 to 366. A new and excellent vacuum-tube oscillator has been developed by Roseveare and Goff. The principle of the Wheatstone bridge and its adaptation to the apparatus used should be thoroughly understood. In this experiment, the conductance of solutions of a typical weak electrolyte and of a typical strong electrolyte are to be studied, at several con-
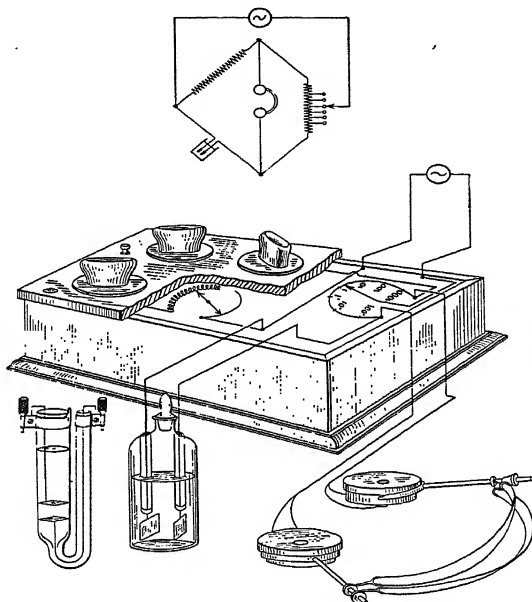

FIG. 39.—Apparatus for determining the electrical conductance of solutions.

centrations. All conductance measurements are made in a thermostat, preferably at 25°C. regulated to 0.02°.

The inexpensive cell shown in Fig. 39, designed by Prof. W. E. Roseveare of this laboratory, is particularly suitable for these measurements. The four corners of the thin platinum squares are anchored tightly by fusion into the pyrex tube. The plates are rigid, the cell is readily filled and emptied, and the volume of solution required is small.

Among the weak electrolytes available are acetic acid, benzoic acid, succinic acid, butyric acid, monochloroacetic acid, ammonium

hydroxide; and among the strong electrolytes are potassium chloride, hydrochloric acid, trichloroacetic acid, etc.

The electrodes of the conductance cell are coated with platinum black as described on page 368. If they have been kept immersed in water, a deposition lasting half a minute is sufficient. If the electrodes are allowed to dry out, it is difficult to rinse out the electrolytes, and it is advisable to dissolve off the deposit in aqua regia (under the hood) and plate out a fresh deposit for about 3 min. The electrodes and cell are rinsed thoroughly with distilled water and then with conductance water (page 444), which has been redistilled so as to remove all impurities including carbon dioxide from the air. The electrodes in the cell are covered with conductance water, and the resistance is determined. The cell is removed, rerinsed, and refilled until the resistance has become constant, showing that any contaminating electrolytes in the cell have been rinsed out. The resistance will be high (of the order of 10,000 ohms or more), and accordingly it is difficult to obtain an accuracy greater than two significant figures. The conductance cells must be handled with care; the electrodes must not be touched with the hands, and they must not be moved with respect to each other during the course of an experiment.

When the cell is clean (as determined by a constant resistance with conductance water), it is rinsed two or three times with a little $0.02N$ potassium chloride solution, and then the resistance is determined with this solution filling the cell. Additional readings are taken, using fresh samples of the solution until successive determinations agree closely. The purpose of these measurements is to secure data for the calculation of the cell constant—to be described in the next section.

The cell is now rinsed with the solution, the conductance of which is to be determined, for instance, the $0.05N$ acetic acid solution. It is a good plan with each solution to fill the cell a second time in order to obtain a check reading and make sure that the cell was thoroughly rinsed.

One hundred milliliters of $0.05N$ acetic acid is prepared by diluting 5.00 ml of $1.0N$ acetic acid with conductance water to 100 ml and checked against a standard. It is used for rinsing and filling the conductance cell and a 50-ml volumetric flask. After the conductance of the $0.05N$ acetic has been determined, the 100-ml volumetric flask is rinsed thoroughly with conductance water and the contents of the 50-ml flask is poured into it. The 50-ml flask is then rinsed with more conductance water into the 100-ml flask, and the diluted solution is brought up to the 100-ml mark with conductance water and mixed thoroughly by pouring back and forth into a clean beaker that has

been rinsed with conductance water and dried. In this way a $0.025N$ solution is prepared for measurement in the conductance cell. It, in turn, is then diluted with an equal volume of conductance water to give $0.0125N$ acid as just described. The dilutions are continued, giving conductance measurements on solutions that are 0.05, 0.025, 0.0125, 0.00625, 0.00312, 0.00156N. The measurements are repeated with potassium chloride solution, to illustrate the behavior of a strong electrolyte. By starting with 50 ml of the $0.02N$ solution, dilutions are made to 0.01, 0.005, 0.0025, and 0.00125N.

Calculations.—The specific conductance of a solution is equal to the reciprocal of its resistance, when measured between electrodes 1 sq cm in area and 1 cm apart. In the usual conductance cell, the distance between the electrodes and the area differ from these dimensions. The specific conductance, however, is related to the measured conductance by a constant factor K, depending upon the dimensions of the cell, which is known as the "cell constant." The cell constant may be determined for a cell by measuring the conductance of a solution of $0.02N$ potassium chloride, or any other solution whose specific conductance is known.

The specific conductance L, for $0.02N$ potassium chloride, is 0.002768 reciprocal ohm at 25°C. If the observed resistance R for the $0.02N$ potassium chloride solution is multiplied by its specific conductance, the cell constant is obtained. Mathematically,

$$K = LR \qquad (2)$$

The specific conductance of any solution may now be calculated, using the same relation and substituting the value of the cell constant and the observed resistance.

The equivalent conductance, the conductance in reciprocal ohms of a solution containing 1 gram equivalent of solute when placed between electrodes of indefinite height placed 1 cm apart, is calculated from the relation

$$\Lambda = \qquad (3)$$

where V is the volume of the solution, in cubic centimeters, which contains the gram equivalent of solute.

The degree of ionization α of the weak electrolyte, at any dilution V, may be calculated from the relation

$$\alpha = \frac{\Lambda}{\Lambda_0} \qquad (4)$$

where Λ is the equivalent conductance measured at the dilution V

and Λ_0 is the equivalent conductance at infinite dilution. In the case of weak electrolytes, the quantity Λ_0 must be calculated from the limiting ionic conductance of the individual ions obtained with the law of Kohlrausch, using strong electrolytes. In the case of strong electrolytes, the value of the limiting conductance is obtained by extrapolating the values of the conductance at finite dilutions to infinite dilution.

The value of Λ_0 at 25° for acetic is 390.8. As a part of this experiment, graphs are plotted showing the relation between equivalent conductance and the square root of concentration for the electrolytes of each type.

The equilibrium or dissociation constant K_D for the weak electrolyte is calculated at each concentration, using equation (1). Mathematical tables of the quantity $\alpha^2/(1 - \alpha)$ for various values of α may be used if desired to shorten the computations. If this calculation for K_D is made for the strong electrolytes, it will be found that a constant is not obtained, indicating that the quantity α, calculated by equation (4), is without significance in these cases.

The data and the results of the experiment may be conveniently tabulated under the following columns: concentration, milliliters containing one mole, resistance in ohms, specific conductance, equivalent conductance, degree of dissociation, and dissociation constant.

Practical Applications.—The later experiments to be described in this chapter are applications of conductance measurements to chemical problems. To illustrate their application to engineering chemistry, it may be mentioned that measurements of this sort have been used to measure the flow of water in streams, to determine the total solids in water, and to test for pollution of water.

Suggestions for Further Work.—The influence of substitution and structure on the dissociation of organic acids may be studied. For example, the dissociation constants of the three chloroacetic acids and propionic acid may be determined and compared with the dissociation constant of acetic acid. In the same way the influence of substituting amino or nitro groups into benzoic acid may be studied.

The conductance behavior of potassium iodide may be studied when dissolved in acetone, in dioxane, in ethanol, and in mixtures of these solvents with water.

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45. Hydrolysis by Conductance Measurements

Theory.—If a salt reacts hydrolytically with 1 mole of water, we have

$$MA + HOH \rightarrow MOH + HA$$
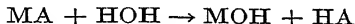
If the reaction goes to completion, the limiting value of the equivalent conductance will be $\Lambda_A + \Lambda_B$, where Λ_A and Λ_B represent the equivalent conductance of the acid and base, respectively.

Furthermore, if Λ is the equivalent conductance of the unhydrolyzed salt, and Λ_h is the experimentally determined equivalent conductance of the partially hydrolyzed salt at the same dilution, then $\Lambda_h - \Lambda$ is the increase in conductance due to the hydrolysis. The value of Λ is found by determining the conductance of the salt in the presence of an excess of one of the products of hydrolysis and subtracting the conductance of the substance added.

Now, if the hydrolysis is complete the increase in the equivalent conductance will be

$$\Lambda_A + \Lambda_B - \Lambda$$

and the degree of hydrolysis x will be given by the expression

$$x = \frac{\Lambda_h - \Lambda}{}$$

Apparatus.—The apparatus used in this experiment is similar to that of Exp. 44; aniline hydrochloride; aniline; conductance water.

Procedure.—The hydrolysis of aniline hydrochloride in water is to be measured quantitatively. An amount 0.004 mole is made up to 100 ml with conductance water in a volumetric flask. After determining the cell constant, the conductance is determined as described in Exp. 44. If a 50-ml volumetric flask is used with the 100-ml flask as described in Exp. 44, the solution is diluted with conductance water to give 0.02 and 0.01 M solutions. The conductance of these solutions is determined also.

The measurements are repeated in the same manner except that the solvent used for making the solution and diluting it is not conductance water, but conductance water that contains aniline dissolved in it, to the extent of 0.04 mole of aniline per liter of aniline-water solution.

Calculations.—By using the equation for the degree of hydrolysis of a salt derived above, the degree of hydrolysis of aniline hydrochloride is calculated at the various concentrations studied. The

equivalent conductances of hydrochloric acid at these concentrations are given in standard tables, or they may be determined experimentally; those of the aniline solutions are, for all practical purposes, negligible.

Aniline hydrochloride is a salt of a weak base and a strong acid. For such a salt, the hydrolysis constant K_h calculated by the formula

$$K_h = \frac{cx^2}{(1-x)} = \frac{K_w}{K_b}$$

where c is the concentration of salt in gram equivalents per liter,

$$K_w = c_{H^+} \cdot c_{OH^-} = 1 \times 10^{-14} \text{ at } 25°C.$$

and

$$K_b = \frac{c_M{}^+ \times c_{OH^-}}{c_{MOH}} = \text{dissociation constant of the base}$$

It is assumed that both the acid and the salt are completely ionized.

If the data of the experiment are used at the several concentrations, the hydrolysis constant of aniline hydrochloride and the dissociation constant of aniline are calculated.

Practical Applications.—The method outlined above is somewhat limited in application. It gives excellent results when the dissociation constant of the weak base (or weak acid) is between 10^{-8} and 10^{-12}, which corresponds to a medium value of the degree of hydrolysis. The method is unsuited to the determination of either very small or very large degrees of hydrolysis. It is evident from the equation that the method is not practical when the difference between the conductance of the hydrolyzed and the unhydrolyzed salt solutions cannot be determined with a fair degree of accuracy.

Suggestions for Further Work.—The hydrolysis of a salt and the dissociation constants increase at higher temperatures. The experimental measurements and calculations may be repeated at 35°. Other salts may be studied such as sodium acetate, glycine-hydrochloride, or sodium cyanide.

Aniline acetate hydrolyzing to give both a weak acid and a weak base offers a more complicated case. It was studied first by Arrhenius, who found that the degree of hydrolysis of a salt of this type is independent of the concentration.

References

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46. Solubility by Conductance Measurements

One of the earlier applications of conductance measurements is illustrated here.

Theory.—In a saturated solution of a difficultly soluble salt, the solution is so dilute that its equivalent conductance may be assumed to be practically equal to the limiting value obtained by extrapolation to infinite dilution; in other words, the effects of interionic attraction are negligible.

If the specific conductance L of the saturated solution and the specific conductance of the water used as solvent are determined, the specific conductance of the ions of the salt may be calculated by simple subtraction.

$$L_{\text{solution}} - L_{\text{water}} = L_{\text{ions}}$$

By assumption and definition the equivalent conductance Λ is given by the expression

$$\Lambda = \Lambda_0 = L_{\text{ions}} \times V \qquad \times \frac{1{,}000}{c}$$

where V is the volume in milliliters holding 1 gram equivalent of solute and c is the concentration in gram equivalents per liter, and Λ_0 is the equivalent conductance at infinite dilution.

Solving for c,

$$c = \frac{1{,}000 L_{\text{ions}}}{}$$

Apparatus.—Same as in Exp. 44, except that a conductance cell with large electrodes placed a short distance apart should be used; lead sulfate or other difficultly soluble salt.

Procedure.—The specific conductance of the water used is determined from resistance measurements, in a cell of known cell constant, at 25°C. The lead sulfate, lead chromate, or silver chloride, whose solubility is to be determined, is shaken repeatedly with the conductance water to remove any soluble impurities. The substance thus prepared is suspended in conductance water and brought to boiling. The resulting solution is filtered (using a well-washed filter paper) into an Erlenmeyer flask of pyrex glass which has been thoroughly cleaned. It is placed in the thermostat at 25° and stirred vigorously until it has come to equilibrium at the temperature of the thermostat. The specific conductance of this solution is determined by repeated measurements on fresh samples of the solution until constant values are obtained.

Calculations.—The solubility of the salt is calculated by means of the equation already given.

Values of Λ_0 are obtained from tables of equivalent conductances (International Critical Tables, vol. VI, page 232), or by adding the ionic conductances involved, using Kohlrausch's law. The concentration c in gram equivalents per liter may be readily changed to grams per liter, or percentage, if desired.

Practical Applications.—This experiment indicates a method by which the solubility of certain difficultly soluble salts may be determined. Although of restricted utility, it serves as a convenient check when applied to the determination of the solubility of certain salts whose analytical determination is difficult. It also serves to check the results of other physicochemical methods.

Suggestions for Further Work.—The solubility of the silver halides, silver chloride, silver bromide, and silver iodide may be determined by using the method outlined above, and the results compared with those recorded in the literature. A very pure conductance water is necessary, and carbon dioxide from the air must be excluded.

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47. Conductiometric Titrations

This experiment illustrates one of the many practical uses of conductance measurements.

Theory.—That the end point of a neutralization reaction involving a strong acid and a strong base may be indicated by conductance measurements will be evident from the following consideration: When the strong base is added gradually to the solution of the strong acid, the fast-moving hydrogen ions are continually being removed to form undissociated water and are replaced by the cations of the base which have an ionic velocity that is not more than one-fifth or one-sixth that of the hydrogen ions. The salt as well as the acid and base are largely ionized, so the difference in conductance is a matter of the different mobility of the ions. The conductance of the solution continues to decrease until all the hydrogen ions disappear (except those present in pure water) *i.e.*, until the acid has been neutralized. If the addition of the base is continued, the conductance of the solution will again increase, because the number of ions in solution will be increased and because of the high velocity of the hydroxyl ions. Best results are obtained when the volume of the solution is not greatly increased during the titration, and, accordingly, the reagent should be concentrated.

The neutralization of a strong base by a strong acid leads in the same way to a minimum conductance at the end point.

When the acid or base is weak, the salt that is formed represses the ionization still further. Under these conditions, the curve may be quite different, but if the addition of reagents is carried out in the right order, it is usually possible to obtain a satisfactory end point. The conductiometric test for an end point is not limited to neutralization reactions; it can be used for precipitations and the formation of complex ions and double salts.

Apparatus.—Wheatstone bridge and accessories, as in Exp. 44; conductance cell suitable for titrations; $1.0M$ solutions of acids and base.

Procedure.—The cell may be made by fusing two platinum wires through the bottom edge of a 250-ml Erlenmeyer flask, attaching copper lead wires and anchoring with sealing wax. A known volume of hydrochloric acid (about 10 ml diluted to 100 ml) is placed in the conductance cell, and its resistance measured in the usual manner. Standard sodium hydroxide solution of approximately equivalent strength is titrated into the cell by means of a burette. After each addition of a small amount of base, the solution is well mixed and its resistance determined. It will be found that the resistance will increase at first, and then, after a certain point, it will decrease. If conductances are plotted against volume of acid added, the end point of the neutralization will be indicated by a sharp minimum in the curve.

If both the acid and base are strong, the titration may be carried out equally well by adding the acid to the base.

When it is desired to neutralize a weak acid, such as acetic acid, the acid must be added to the base. The hydroxyl ion is then replaced by the slower moving anion of the acid, and the conductance of the solution is decreased. Since the acid is but slightly ionized, and this ionization is reduced by the presence of the neutral salt, the excess of acid added does not increase the conductance. The neutral point is indicated by a sharp change in slope of the conductance curves. If the base is added to the weak acid, the end point will not be sharp.

In the second part of the experiment, then, a known volume of the base is measured into the conductance cell and titrated with the acetic acid solution.

Calculations.—The results of the experiment are most readily presented in the form of curves in which the number of milliliters of titrating solution are plotted as abscissas against either resistance or

its reciprocal (conductance), as ordinates. The former will show a maximum, the latter a minimum, in the curve.

Practical Applications.—Conductiometric titration has been applied successfully to a number of problems in chemical research. It was used by Tosterud[3] to study the formation of compounds between the alkali fluorides and aluminum fluoride similar to the well-known salt $3NaF \cdot AlF_3$. The formation of complex ions in solution has been studied in a number of cases, using the method of this experiment.

The method is particularly useful in determining the end point of a reaction in colored or turbid solutions. This is illustrated by the work of Harned[4] on the quantitative determination of copper and nickel sulfates in solution.

The conductiometric method may be applied to the determination of the end points of analytical precipitations. It is particularly suited to the determination when the precipitate formed is soluble to an appreciable extent in the solution, a fact that would cause a low result by the ordinary gravimetric method depending on precipitation but which is often without influence upon the end point as determined conductiometrically. As an illustration, the concentration of Ba^{++} ions or Pb^{++} ions in solution may be determined by solutions containing known amounts of $Cr_2O_7^{--}$ ions or SO_4^{--} ions.

Suggestions for Further Work.—The titration discussed under Practical Applications provides a number of suggestions for further work.

A method that uses the current passing through a dropping mercury electrode in the solution has been stressed by Kolthoff.[5]

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CHAPTER XI

ELECTROMOTIVE FORCE

48. Single-electrode Potentials

In this experiment exact measurements are made on the potential difference between a metal and a solution of its ion. Practice is obtained in the use of the potentiometer.

Theory.—It is convenient to regard the electromotive force of an electrochemical cell as the sum of two single-electrode potentials. By the latter term we mean the potential of an electrode against a solution of its ions. The single potential of a metal in normal and unstrained condition will vary with the activity of the metal ion in the solution surrounding the electrode. Further, any process that causes a decrease in concentration of the positive metal ions about an electrode causes the single-electrode potential of the metal to become less positive.

The potential of an electrode against a solution of its ions is a measure of the tendency of this metal to detach electrons. There is at present no absolute way in which this tendency can be measured, but for two metals it can be compared. In order to assign numerical values to single-electrode potentials, it is necessary to choose some arbitrary zero. There is now in use a widely accepted convention which assigns the value *zero* to the standard hydrogen electrode, in other words, a hydrogen electrode dipping into a solution in which the activity of the hydrogen ions is unity when solution and electrode are in equilibrium, with hydrogen gas at a partial pressure of 1 atm.

If a metal electrode is immersed in a solution containing the ions of that metal, the electrode reaction is

$$^- + ne = M \tag{1}$$

where n is the valence of the metal and e is the faraday of electricity (electrons). The ability of a metal electrode to detach electrons will be a function of the metal-ion concentration. The relation between the single-electrode potential, at unit activity of ions $E_M{}^0$ (the standard electrode potential) and the potential of the electrode in a solution of its ions at any activity E_M may be obtained by making use of a

chemical cell in which one of the electrodes is the normal hydrogen electrode. The cell is set up as follows:

$$H_2 \text{ (1 atm.), } H^+(a = 1) \| M^{n+}, M$$
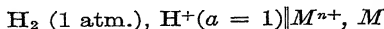
The reaction per faraday in the cell is

$$\frac{1}{2} H_2 + \frac{1}{n} M^{n+} = H^+ + \frac{1}{n} M \tag{2}$$
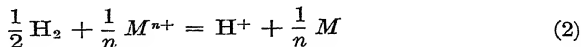
The total reaction of the cell is the result of the addition of two electrode processes. According to convention, the reaction is written in such a way that it will cause electrons e to flow from right to left within the cell, *i.e.*, the reaction $\frac{1}{2}H_2 \rightarrow H^+ + e$ leaves electrons at the left, and the reaction

$$M^{n+} + e \rightarrow \frac{1}{n} M$$
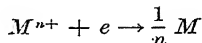
takes electrons from the electrode at the right.
The corresponding electromotive force is

$$E = E^0 - \frac{R'_1}{F} \ln \frac{a_{H^+} \cdot a_M^{\frac{1}{n}}}{a_{H_2}^{\frac{1}{2}} \cdot a_{M^{n+}}^{\frac{1}{n}}} \tag{3}$$

where a is the activity or effective concentration. The solid metal, the hydrogen gas at 1 atm., and the hydrogen at an effective concentration of 1 mole of hydrogen ions per liter are all taken as unit activity by convention. Therefore

$$E = E^0 + \frac{RT}{n\mathbf{F}} \ln a_{M^{n+}} \tag{4}$$

Apparatus.—Potentiometer; electrodes of cadmium, copper, lead, silver, and zinc; electrode vessels; calomel electrode ($1N$ potassium chloride); standard cell; dry cells; key; $0.100M$ solutions of cadmium chloride, copper sulphate, lead nitrate, silver nitrate, zinc sulfate; $2N$ ammonium nitrate solution; 100-ml volumetric flask; one 10-ml pipette.

Procedure.—In this experiment the single–electrode potentials of cadmium, copper, lead, silver, and zinc are to be determined in $0.1M$ and $0.01M$ solutions. The $0.1M$ solutions are prepared carefully by weighing out the salts with due allowance for water of crystallization, or by determining the concentration by analytical methods. The $0.01M$ solutions may be prepared by pipetting exactly 10 ml of the $0.1M$ solution into a volumetric flask and diluting with distilled water.

The electrodes of copper, zinc, and lead are prepared by pouring the molten metal from a small porcelain crucible into a glass tube and setting a copper wire into the upper end for a terminal. When cold the glass tube is broken away and removed. For the copper electrode a wire of large diameter is used. All these electrodes are amalgamated to give a steady potential less affected by mechanical strains. The electrode is placed in a beaker of dilute acid with a drop of mercury, and a small brush or cloth is used to spread the mercury over the surface of the electrode.
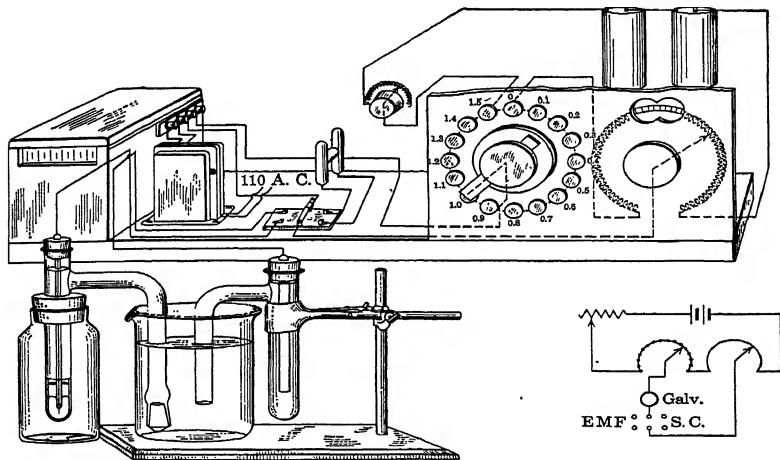
Fig. 40.—Measurement of electrode potentials with the potentiometer.

The silver electrode is prepared by electroplating spongy silver on a platinum-wire cathode in a silver cyanide (**caution!**) solution. A single dry cell gives sufficient voltage.

For best results the aqueous solutions should be bubbled out with a stream of hydrogen, to remove dissolved oxygen.

The electrodes are mounted in rubber stoppers and set tightly into vessels having side arms to provide liquid contact with a reference electrode. The snugly fitting stopper prevents the solution from siphoning out of the electrode vessel.

A normal calomel electrode is used for the reference electrode, and the connecting arms of the two electrodes are placed in a small beaker containing $2N$ ammonium nitrate solution. This solution (called a

"salt bridge") is used to minimize the liquid-junction potentials and, in certain cases, to prevent precipitation, *e.g.*, silver chloride. The electromotive force of this cell is determined by means of the potentiometer, connected as shown in Fig. 40.

It is important to note in which direction the current is flowing and to record which is the positive electrode, *i.e.*, the electrode connected to the positive terminal of the potentiometer when the circuit is balanced. If the galvanometer always deflects in the same direction no matter how the potentiometer is set, the terminals of the unknown cell must be reversed to obtain a point of balance.

Calculations.—In order to simplify the calculations, the single-electrode potential of the calomel cell is taken as zero. The single-electrode potential of the metal in question is then given directly by the voltage read on the potentiometer at the point of balance, and the electrode is negative if it is connected, as in the case of zinc, to the negative terminal. Negative electricity (electrons) is then flowing from the solution to the electrode. Again if it is connected to the positive electrode, as in the case of silver, it is positive, and negative electricity is flowing from the electrode to the solution.

Since the normal calomel electrode is positive with respect to the standard hydrogen electrode by 0.2805 volt (at 25°C.), if +0.2805 volt is added algebraically to the values obtained with the normal calomel electrode, the single-electrode potentials of the metals are obtained in solutions of their ions at the specified concentration, referred to the standard hydrogen electrode.

From these values of E it is possible to calculate the standard electrode potentials E^0, using equation (4), and the activities $a_M{}^{n+}$ obtained by multiplying the molarity of the dissolved salt by the mean activity coefficient of the electrolyte.

MEAN ACTIVITY COEFFICIENTS OF ELECTROLYTES AT 25°C.

Electrolyte	Concentration		
	0.001M	0.01M	0.1M
Cadmium chloride.........................	....	0.53	0.22
Copper sulfate............................	0.69	0.40	0.16
Lead nitrate..............................	0.89	0.69	0.37
Silver nitrate............................	0.95	0.90	0.72
Zinc sulfate..............................	....	0.40	0.16
Sodium chloride..........................	....	0.90	0.78
Hydrochloric acid........................	....	0.90	0.80

In these calculations it is assumed that the hydrogen-ion activity is equal to the square root of the mean activity of hydrochloric acid. Practical results are obtained in this way, but there is some uncertainty concerning the absolute significance of a single-electrode potential measured against ions of only one charge.

A few of the activity coefficients are given in the table on page 190.

The value of the standard electrode potential for each of the five metals studied is calculated and compared with the values given in the following table.

STANDARD ELECTRODE POTENTIALS AT 25.0°

Electrode	Normal calomel = 0	Normal hydrogen = 0
Na+, Na.	−2.9951	−2.7146
	−1.0423	−0.7618
Cd++, Cd.	−0.6818	−0.4013
Pb++, Pb.	−0.403	−0.122
H+, H₂...	−0.2805	0.0000
Cu++, Cu.	+0.0636	+0.3441
Ag+, Ag..	+0.5173	+0.7978
Cl−, Cl...	+1.0778	+1.3583

These single-electrode potentials may be combined to give a voltaic cell, thus

$$E_{cell} = E_- + E_+$$

where E_+ is the single-electrode potential of the positive pole of the cell and E_- is the single-electrode potential of the negative pole of the cell.

The voltage of a cell is regarded as the algebraic sum of the single-electrode potentials when care is taken to make the order in which the electrolyte and electrode are written the same as that in which they appear in the cell. Thus, unless noted to the contrary, the two electrode potentials are written in opposite order. For example, the potential of the cell

Zn, Zn++|Cu++, Cu
+0.7618 +0.3441
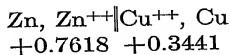
is 1.1059, the standard potential of the zinc being positive because the cell is written Zn, Zn++ instead of Zn++, Zn as in the table.

Practical Applications.—If the standard electrode potentials of the metals studied are arranged in order, the metals will be found to fall into their respective

positions in the electromotive-force series.   If the strongly electronegative metals are placed at the top of the series, each metal in the list will throw out of solution the metals that lie below it in the series.

When the value of E^0 is known, it is a simple matter to calculate the activity of the ions from the measurement of E in a given solution, using equation (4). This method of determining activities finds many important uses.

Suggestions for Further Work.—It is of interest to study the effect of continued dilution of the metallic ions about an electrode upon its single potential.   It has been suggested in the experiment that $0.01M$ and $0.1M$ salt concentrations be used.   By making further careful dilutions of these solutions, it will be found that the values of the single-electrode potential becomes less positive.

The effect on the single-electrode potential of bending or straining the electrode is sufficient to be measured by means of the student potentiometer, except in the case of the softest of the metals.

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49. Measurement of H^+ Ion Activity.   The Hydrogen Electrode and the Quinhydrone Electrode

This experiment illustrates the practical use of the electrochemical determination of activities and gives practice in potentiometric titrations, in the use of the hydrogen and the quinhydrone electrode, and in the calculations of pH.

The determination of the absolute activity of an ion in solution is uncertain on account of the potential that exists when two different solutions are in contact.   The salt bridge of potassium chloride minimizes this error.   The potentiometric method for determining the effective acidity or hydrogen-ion activity is very important for many practical purposes in biology and industry as well as in chemistry.

<div align="center">

The Hydrogen Electrode

</div>

Theory.—For the cell

$$H_2 \text{ (1 atm.)} | HCl | HCl | H_2 \text{ (1 atm.)}$$

the electromotive-force expression can be written in the form

$$E = \frac{RT}{F} \ln \frac{a_{H^+,2}}{a_{H^+,1}} + E_j \qquad (1)$$

Here, $a_{H^+,1}$ and $a_{H^+,2}$ are the activities of the hydrogen ion on the two sides of the cell and E_j is the liquid-junction potential. If we knew E_j and if $a_{H^+,2}$ were extremely small, so that it could be taken as equal to the molality, the activity of the hydrogen ions in the more concentrated solution $a_{H^+,1}$ could be determined. The nearest approach to the solution of the first difficulty, the use of a salt bridge between the solutions to "eliminate" the junction potential, is sufficiently good for all practical purposes. In this event, the working cell can be represented as follows:

$$\text{H}_2 \text{ (1 atm.)} \left|\underset{a_{H^+,1}}{\text{H}^+}\right\|\underset{a_{H^+,2}}{\text{H}^+} \text{ H}_2 \text{ (1 atm.)}$$
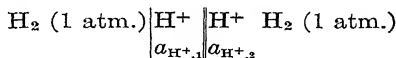
If the hydrogen-ion activity $a_{H^+,2}$ is fixed at unity (standard hydrogen electrode), the right-hand element of the cell serves as reference electrode. To this half-cell there has been assigned the value zero. Then, as the hydrogen-ion activity in the other element is changed, the electromotive force of the cell as a whole will vary, as required by the equation

$$E = \frac{RT}{F} \ln \frac{a_{H^+,2}}{a_{H^+,1}} = - \frac{RT}{F} \ln a_{H^+,1} \qquad (2)$$

In the laboratory, it is more convenient to use a calomel electrode than the normal hydrogen electrode. The computations are not more difficult because the potentials of the several calomel electrodes ($0.1N$ potassium chloride, N potassium chloride, or saturated potassium chloride), with respect to the normal hydrogen electrode, are known with considerable certainty. Thus, for the cell in which the normal calomel electrode is used,

$$\text{H}_2 \text{ (1 atm.)} \left|\underset{a = 1}{\text{H}^+}\right\| N \text{ KCl, Hg}_2\text{Cl}_2 \big| \text{Hg}$$
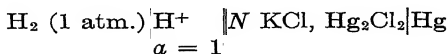
the voltage is

$$E = E_1 + E_2 = 0 + 0.2805 = 0.2805.$$

The laboratory cell is

$$\text{H}_2 \text{ (1 atm.)} \big| \text{H}^+ \| N \text{ KCl, Hg}_2\text{Cl}_2 \big| \text{Hg}$$
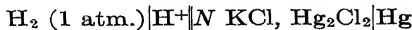
and

$$E = \frac{RT}{F} \qquad 0.2805 \qquad (3)$$

This is the formula that gives the relationship between the hydrogen-ion activity and the voltage of the laboratory cell.

Apparatus.—Potentiometer; dry cells; key; standard cell; galvanometer (box type); hydrogen electrode; platinum chloride; calomel electrode; 0.5N hydrochloric acid (with normality accurately known); 0.5N (approximate) sodium hydroxide and sodium carbonate.

Procedure.—A diagram of the apparatus is given in Figs. 40 and 41. The student should be familiar with the wiring diagram and the
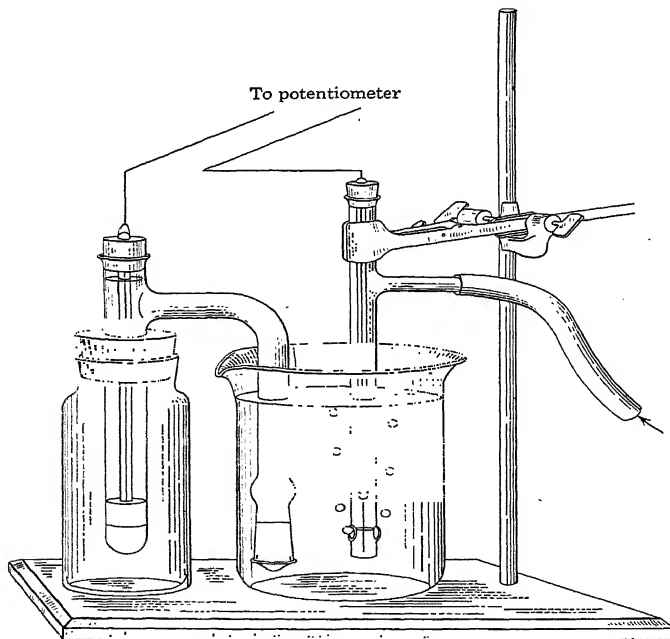
FIG. 41.—Hydrogen electrode.

principle of the potentiometer before starting the experiment. (A voltmeter, galvanometer, and resistance may be used in place of the potentiometer.)   The hydrogen electrode is connected to the negative

terminal of the potentiometer, and the normal calomel electrode described on page 373 is connected to the positive terminal. The circuit is closed only momentarily with the tapping key until the point of balance is found because any appreciable passage of current will polarize the hydrogen electrode and any considerable amount of current will affect the potentials of the calomel electrode and the standard cell.

The hydrogen electrode proper consists of a piece of platinum wire, or foil, the surface of which is coated with finely divided platinum and saturated with gaseous hydrogen. The wire is fused to a copper wire and sealed through a glass tube. This tube is provided with a jacket arranged so that hydrogen may be supplied to the electrode. To prepare the electrode, it is wiped as clean as possible and dipped for a few seconds into warm aqua regia, under the hood. The electrode is then platinized, *i.e.*, coated with a deposit of platinum black, by connecting the electrode to the negative pole of two dry cells connected in series. Another platinum wire serves as the anode. The electrodes are placed in a 1 per cent solution of platinic chloride, and the electrolysis is allowed to continue for several minutes. The electrodes are then placed in a small beaker of distilled water to which a drop of concentrated sulfuric acid has been added, and the electrolysis is allowed to proceed as before. This treatment produces hydrogen and removes any impurities. The electrode should be kept in distilled water until used; it should never be allowed to dry out. Electrodes must be replatinized from time to time as the coating of platinum black becomes "poisoned" with use.

Hydrogen from a tank is purified by passing through a solution of alkaline pyrogallic acid and one of potassium permanganate and washed with water. Unless found to be free from sulfur, all the rubber tubing used should be boiled in concentrated sodium hydroxide solution and rinsed.

There are a number of neutralization reactions that may be studied by means of the hydrogen electrode. For example, 25 ml of $0.5N$ hydrochloric acid, of accurately known normality, is placed in a small beaker and enough water is added to cover the holes of the glass hood which surrounds the platinized wire. The electrode is set opposite the holes and adjusted so that the wire is partly immersed in the solution and partly surrounded by the hydrogen gas. It is set at such a level that there is at least 1 cm of the solution above the holes to prevent air diffusing back into the region of the electrode. The initial voltage should be approximately 0.32 volt; otherwise the electrode is not functioning properly. Replatinizing the electrode will usually

correct faulty · behavior of a hydrogen electrode. When properly platinized a steady voltage should be reached in half a minute or so.

Approximately 0.5N sodium hydroxide is added slowly from a burette, and the solution is stirred after each addition. At first about 5 ml is added at a time, but as the neutral point is approached readings are taken more frequently, and after passing the end point larger amounts can again be added. The exact end point should be found by accurate drop-by-drop titrations so that the pH at which the indicator changes color can be calculated. The addition of alkali is continued until the voltage has become practically constant.

The hydrogen electrode is next placed in 25 ml of the 0.5N sodium carbonate solution and the voltage of the cell determined. It should be approximately 0.95 volt. The 0.5N hydrochloric acid solution is titrated into this solution. Phenolphthalein is added at first, and when this becomes colorless, methyl orange is added. The exact points at which the indicators turn are recorded.

Calculations.—Curves are drawn in which the numbers of milliliters of titrating solution added are plotted as abscissas against voltages as ordinates. The steepest parts of the curves correspond to the end points. They are used for calculating the normality of the sodium hydroxide and the sodium carbonate from the known normality of the original hydrochloric acid solution.

The working equation (3) at 25° becomes

$$E = 0.0591 \log \cdot \quad + 0.2805$$

Therefore

$$\log a \quad = \frac{E - 0.2805}{0.0591} \tag{5}$$

The hydrogen-ion concentration of a given solution may be calculated by means of this equation from the observed voltage E of the cell. In these calculations, a_{H^+}, is expressed in gram ions per liter.

Following the suggestion of Sörensen, hydrogen-ion activities are commonly expressed in terms of pH values. The relation between the two modes of expression is given by equation (6)

$$- \log a_{H^+} = pH \tag{6}$$

Thus, in a neutral solution, $a_H^+ = 10^{-7}$, or pH 7. The pH of a solution at 25° is calculated from the voltage by equation (7)

$$pH = \frac{E - 0.2805}{0.0591} \tag{7}$$

The hydrogen-ion activities and pH values corresponding to the voltages at which the indicators phenolphthalein and methyl orange change color may now be calculated.

Practical Applications.—The applications of the hydrogen electrode to chemistry and to research are indeed numerous. It would be impossible in a book of this kind to include even a typical list of its uses, for although the cataloguing of a great number of neutralization reactions might represent its application to analytical chemistry, it would leave other fields of at least equal importance quite untouched. Rather, the student is urged to consult the list of references appended to this experiment, where, in addition to theoretical discussions, detailed information concerning the use and application of the hydrogen electrode is given.

Colorimetric estimation of pH with indicators finds extensive use in biochemistry, biophysics, bacteriology, and related sciences. Such biological phenomena as the stability of proteins, the effectiveness of enzymes, and the growth of microorganisms depend greatly on the pH of the system, and in proper laboratory experiments this factor is always made subject to rigid control. This method of measurement of pH also is finding wide application in industrial and municipal laboratories. Directions for the preparation of solutions of selected indicators and the comparison of the indicator color with the pH value of the solution are given on page 441.

Suggestions for Further Work.—Titrations may be made with other acids and bases such as acetic, boric, and phosphoric acid and ammonium hydroxide. If oxygen or air is used instead of hydrogen, similar titration curves are obtained. The end point can be determined satisfactorily but the "oxygen electrode" is not reversible. Accordingly, it is not possible to apply thermodynamical calculations. Irreversible electrodes give potentials that are less steady.

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THE QUINHYDRONE ELECTRODE

Theory.—The quinhydrone electrode has been applied to the determination of hydrogen-ion activities in acid solution with marked

success.   It makes use of the oxidation-reduction reaction

Hydroquinone   Quinone
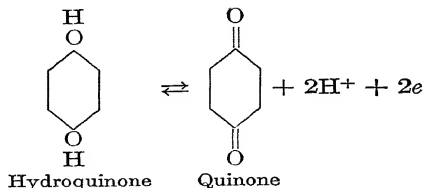
The oxidation potential of this system is given by the equation

$$= E^0 + \qquad \log \frac{a_Q}{a_{QH}} + 0.0591 \log a_{H^+} \tag{8}$$

It happens that quinone and hydroquinone combine to form a chemical compound quinhydrone, containing one mole of each of the reactants.   Adding quinhydrone crystals to a solution then is equivalent to adding equivalent amounts of quinone and hydroquinone—and it is much easier than weighing them out.   When quinhydrone is introduced into a solution, it dissociates slightly giving equal concentrations of quinone and hydroquinone.   Then a_Q/a_{QH_2} is unity, $\log a_Q/a_{QH_2}$ becomes zero, and

$$E = E^0 + 0.0591 \log a_{H^+} \tag{9}$$

That is, the potential of the quinhydrone electrode changes with change in hydrogen-ion activity, in a manner which is exactly similar to that of the hydrogen electrode.

The value of E^0 at 25°C. has been determined by a number of investigators, and found to be 0.6990 volt, measured against a normal hydrogen electrode.   When the normal calomel electrode is used, the working equation becomes

$$- \log a_{H^+} = \text{pH} = \frac{0.6990 - 0.2805 - E}{0.0591}$$

$$\frac{0.4185 - E}{0.0591} \tag{10}$$

The quinhydrone electrode has already established itself as a practical instrument for the determination of hydrogen-ion activity. It has several advantages over the hydrogen electrode: it may often

be applied in cases where the hydrogen electrode canno
comes to equilibrium very rapidly, and its manipulation is much more
convenient. Its one serious drawback is the fact that on account of a
chemical oxidation reaction it cannot be used in alkaline solutions
having a pH greater than 8.

Apparatus.—Potentiometer with accessories; bright platinum electrode; quin-
hydrone; 0.5N NaOH and 0.5N acetic acid.

Procedure.—The apparatus is the same as shown in Fig. 41, except
that a bare, shiny platinum wire is used instead of the platinized
platinum wire and hydrogen hood.

The solution whose hydrogen-ion activity is to be determined is
placed in a small beaker, a small pinch of quinhydrone sufficient to give
a saturated solution is added (0.1 g), and the solution is stirred vigor-
ously. Mechanical stirring with a small motor is sometimes helpful.
Measurements of the electromotive force of the cell are taken until a
constant value is obtained. The cell may be represented in the follow-
ing manner:

$$\text{Hg} \mid \text{Hg}_2\text{Cl}_2, \, N \, \text{KCl} \mid \text{acetic acid solution, quinhydrone} \mid \text{Pt}$$
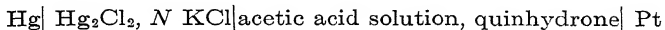
The platinum quinhydrone electrode is connected to the positive
terminal of the potentiometer in concentrated acid solutions, but when
an excess of alkali is added it may be necessary to reverse the terminals
in order to obtain a point of balance.

If quinhydrone is not available it may be prepared, as follows:
Three hundred grams of ferric ammonium sulphate is dissolved in
300 ml of water at 65°C. This solution is poured into a warm solution
of 25 g of hydroquinone in 300 ml of water. Quinhydrone precipitates
in fine dark needles. The mixture is cooled in ice water and filtered
by suction. The precipitate of quinhydrone is washed with cold
water. For work of the highest degree of accuracy, the quinhydrone
should be recrystallized from water.

The use of the quinhydrone electrode is illustrated with the titra-
tion of acetic acid by sodium hydroxide. Twenty-five milliliters of
approximately 0.5N acetic acid is placed in a small beaker, and the
bright platinum electrode and the lower end of the bridge arm of the
calomel electrode are immersed in the solution. The 0.5N sodium
hydroxide is added until the neutral point has been passed, using 5-ml
portions at first and finishing with drop-by-drop additions at the
neutral point. The initial voltage and the voltages after each addition
of sodium hydroxide are recorded.

From time to time it is necessary to clean the bright wire electrode. This is most readily accomplished by heating the wire in an *alcohol* flame.

Calculations.—A graph is drawn in which the voltages are plotted against the volume of the sodium hydroxide added. The end point corresponds to the titrations that give the steepest part of the curve. When the normality of the sodium hydroxide is known, the normality of the acetic acid is calculated.

When equation (10) is used, the activity of the hydrogen ions and the pH value may be calculated for a number of the observed voltages taken from the titration curves. These calculations are limited, of course, to solutions whose hydrogen-ion activity is greater than 10^{-8} or, in other words, whose pH value is less than 8.

Practical Applications.—The quinhydrone electrode may be extensively applied in the determination of acidity. It may be used in most cases as a substitute for the hydrogen electrode; in addition, it makes possible, within limitations, the determination of the acidity of solutions containing metals that lie below hydrogen in the electromotive-force series. For example, it has found use in the determination of the acidity of nickel- and copper-plating solutions. It has been applied with distinct success to the determination of the acidity of soils, to the determination of the pH of lake waters at different depths, and to the titration of alkaloids and their salts.

Suggestions for Further Work.—The influence of the addition of metallic salts on the hydrogen-ion activity of an acid may be investigated. The addition of sodium chloride to hydrochloric acid solution, for example, causes an increase in the effective acidity of the solution. The quinhydrone electrode provides a method for the determination of the hydrogen-ion activity of sulfuric acid solutions to which varying amounts of copper sulfate or nickel sulfate have been added.

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   Additional references are given under the hydrogen electrode.

### 50. Oxidation-reduction Potentials.   Potentiometric Titrations

The important relation connecting electromotive force with concentration is applied to two oxidation-reduction reactions and one precipitation reaction. The practical applications in analysis are apparent. Indicators that change color at definite oxidation-reduction potentials are illustrated.

Theory.—A potentiometric titration is one in which the end point is detected by measuring the change in potential of a suitable electrode during the titration. The electrode whose potential indicates the change in activity or concentration of the ion being titrated is called the "indicator electrode."

When a substance takes on electrons it is reduced, and when it loses electrons it is oxidized. Reduction occurs, then, at the cathode where the electrons are transferred from the cathode to the surro ions, leaving the electrode positively charged, and oxidation where the ions give up electrons at the anode.

The determining factor in the potential of the indicator electrode is the ratio of the activities a or effective concentrations of the oxidized and reduced forms of the ion. A general reduction reaction for positive ions I may be written

$$I^{n+} + e = I^{(n-1)+}$$
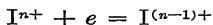
where e is an electron and n is the number of positive charges that the ion possesses in the oxidized form. The formula giving the electrode potential E for any mixture of these oxidized and reduced ions is

$$RT \atop a_I{}^n \tag{1}$$

where E^0 is the standard electrode potential, *i.e.*, the potential that is obtained when the two ions are present in equal amounts.

This equation is of fundamental importance because it connects chemical equilibria and electrochemical measurements with reversible electrodes. It is useful in determining the concentration of ions. In titration curves the equation itself determines the shape of the curve and the numerical value of E^0 determines its position on the potential scale.

In order to use this equation quantitatively it is necessary to have reversible electrodes, but the end point in a titration curve can be determined empirically without the use of this theoretical equation and with electrodes that are not necessarily reversible. Under these conditions the end point is indicated by a rapid change in voltage when a small amount of reagent is added. The steepest part of the curve, when voltage is plotted vertically against the number of milliliters of reagent added, indicates the point at which the two reactants are present in chemically equivalent amounts.

In a precipitation reaction the potential of the indicator electrode remains constant as more of the titrating solution is added because the concentration is fixed by the solubility. When all the material has been precipitated, however, the concentration of the added ions increases sharply and the electrode potential registers a sudden change.

Apparatus.—Sliding contact rheostat; voltmeter; portable galvanometer; two dry cells; bright platinum electrode; electrical key; calomel electrode; two burettes;

500 ml of 0.01M ferrous sulfate, 250 ml of 0.01M ferric sulfate, 500 ml of 0.01M potassium dichromate, each being also approximately hundredth normal in sulfuric acid; 100 ml of 0.01M zinc sulfate; 100 ml of 0.01N potassium ferrocyanide; dilute potassium ferricyanide; diphenylamine; orthophenanthroline-ferrous ion.

Procedure.—The arrangement of apparatus and the electrical connections are given in Fig. 42. The voltage picked off with the rheostat is varied until the galvanometer registers zero, showing that it is equal and opposite to the potential of the platinum wire against
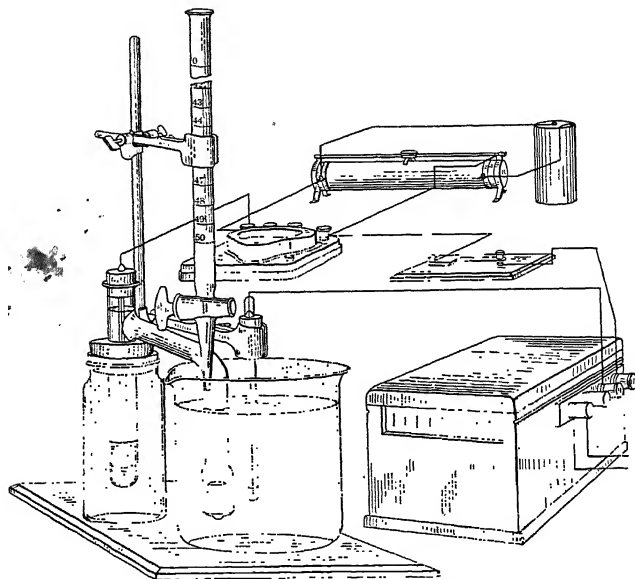
Fig. 42.—Potential measurements with a voltmeter.

the calomel electrode. The electrode potential may be referred to the hydrogen electrode as zero by adding 0.2805 volts, if it is desired to compare the potentials with standard values.

The validity of equation (1) is first checked with mixtures of ferric and ferrous ions in different ratios. The volume of solution surrounding the platinum wire is kept at 50 ml, using ferrous and ferric sulfate solutions (acidified to prevent hydrolysis) in the following quantities run out from burettes: 5 to 45, 10 to 40, 20 to 30, 25 to 25, 30 to 20, 40 to 10, and 45 to 5. After thorough stirring the voltage is read and recorded.

In a second experiment the oxidation of ferrous sulfate by potassium dichromate is followed. Twenty-five milliliters of the ferrous sulfate is placed in the beaker, a few milliliters of concentrated hydrochloric acid is added, and the potassium dichromate is titrated into the beaker from a burette with vigorous stirring. At first several milliliters are added at a time, but, as the point of equivalence is approached, smaller and smaller volumes are added. The potential rises slowly at first, then rapidly and then slowly again after the dichromate is present in excess. The voltages and burette readings are recorded for graphing.

A second set of readings may be taken in which 25 ml of the potassium dichromate is placed in the beaker and titrated with the ferrous sulfate in the burette.

Colored indicators are available for oxidation and reduction similar to indicators that are used for acids and alkalis. They change color at definite oxidation potentials just as the acid indicators change at definite hydrogen ion activities. Often they find important uses in biochemical problems. Their use is not extensive as yet, perhaps because each indicator is adapted to relatively few reactions.

The application of such indicators may be illustrated by diphenylamine,[9] first used for this purpose by Knop. When it is oxidized to give a compound which may be reduced to diphenyl benzidine the color is changed from pale green to intense blue. Ferric ions tend to produce the blue color because the oxidation potential is so close to that of the ferrous-ferric system. However, if the ferric ions are removed as fast as formed by having phosphoric acid present, the blue color is not produced until all the ferrous ion in solution has been oxidized by the dichromate. The potential at which this color change occurs is recorded and converted into the standard potential against the standard hydrogen electrode.

Another indicator that is useful in the study of the reaction between ferrous iron and dichromate solution is orthophenanthroline-ferrous ion. The red complex ferrous ion is oxidized to the pale blue complex ferric ion at a relatively high level on the oxidation-reduction scale. The color change is relatively slow when titrating with the dichromate solution, but sharp and distinct in the reverse titration. Directions for the preparation of the indicator are given in the original article of Walden, Hammett, and Chapman,[10] who introduced the indicator for this titration.

For a third experiment the precipitation of zinc with potassium ferrocyanide is suggested. Twenty-five milliliters of 0.01M zinc sulfate is placed in the beaker in contact with the bright platinum electrode

as shown in Fig. 42. A few drops of a dilute solution of potassium ferricyanide is added. The $0.01N$ potassium ferrocyanide is titrated into the solution of zinc. The ratio of oxidizing ferricyanide ions to reducing ferrocyanide ions is kept constant by virtue of the fact that the latter is continually precipitated out as zinc ferrocyanide. The potential of the platinum wire, which depends on the ratio of the number of collisions of reducing and oxidizing ions, remains constant until all the zinc has been precipitated. Then the next addition of ferrocyanide increases the number of ferrocyanide ions, and the voltage decreases. Further additions give further decreases. From the number of milliliters added up to the time of a definite increase in voltage, the amount of zinc in solution can be calculated.

The solution is stirred vigorously after each addition and time allowed for a steady potential to be attained. The titration may be carried out at room temperature, but equilibrium is more rapidly attained if the solution is heated to about 60°.

Calculations.—The standard electrode potential E^0 for the ferrous-ferric ions is calculated with the help of equation (1), using the concentrations in moles per liter instead of the activities. This calculation can be accurate only in so far as the activity coefficient for the ferrous and ferric iron are the same. Furthermore, the potential is somewhat affected by the sulfuric acid present. Nevertheless a fairly consistent value of E^0 is obtained over the wide changes in concentration. This value of E^0 is compared with the accepted value found in tables.

The titration curves for the ferrous sulfate and potassium dichromate are plotted, voltages against the number of milliliters added, and the end point determined from the steepest part of the curve.

A second graph is prepared in which $\Delta E/\Delta C$ is plotted against C where E represents the potential and C the total number of milliliters. The quantity $\Delta E/\Delta C$ is a maximum at the equivalence point. This equivalence point may be checked, if desired, with spot plate indicators used in volumetric analysis.

The voltages at which the oxidation-reduction indicators change color are compared with the accepted voltages as given in tables.

The titration curves for zinc sulfate and potassium ferricyanide and ferrocyanide are graphed, plotting voltages against the number of milliliters added, and the end point is determined.

Practical Applications.—Potentiometric titrations can be carried out advantageously for many oxidation, reduction, or precipitation reactions. They are usually more accurate than titrations depending on other volumetric indicators, and they can be used when no other suitable means of titration are available.

They can be used equally well in clear, colored, or turbid solutions. Acid titrations are given on page 195.

Suggestions for Further Work.—Among other systems that may be studied with a reversible electrode to determine E^0 may be listed stannous-stannic ion, cobaltous-cobaltic ion, and quinone-hydroquinone.

Among other systems that illustrate potentiometric titration are the oxidation of stannous chloride by potassium dichromate and the oxidation of ferrous sulfate with potassium permanganate.

Bimetallic electrodes, such as platinum and tungsten electrodes, may be used instead of platinum and a calomel cell. One electrode polarizes more than the other, thus creating a difference in potential depending on the concentration. The precipitation of lead nitrate by ferrous sulfate may be followed by using a small amount of ferric sulfate with the lead salt.

Other oxidation-reduction color indicators are toluidene blue, phenosafranine, methyl violet, and indigo carmine.

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51. The Glass Electrode—Titration Curve of a Typical Protein

The use of the glass electrode for industrial operations is increasing very rapidly. Improvements in electron tube circuits and in the glass electrode itself have been partly responsible for its popularity. In this experiment it is used in connection with the behavior of a protein which is of interest in biochemistry.

Theory.—For many solutions, the glass electrode appears to be the only electrode suitable for the determination of hydrogen-ion activity. It functions in both oxidizing and reducing media, and it seems to give a proper result in the case of colloidal systems where other electrodes have failed almost completely. The action of the electrode is not

entirely understood. It is believed, in some quarters, that the glass membrane is permeable and reversible to hydrogen ions throughout. According to others the hydrogen ions are adsorbed on the surface of the glass. In either case, the following arrangement should act as a concentration cell in hydrogen ions:

$$Hg \,|\, Hg_2Cl_2, \, N \text{ KCl} \,\|\! \left.\begin{matrix} H^+ \\ a_{H^+,1} \end{matrix}\right| \text{Glass} \left|\begin{matrix} H^+ \\ a_{H^+,2} \end{matrix}\right.\!\| N \text{ KCl, } Hg_2Cl, \; Hg$$
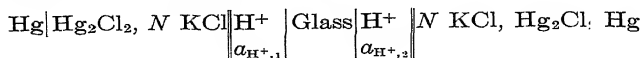
Since the effect of two calomel electrodes cancels, the electromotive force of such a cell would be

$$E = \frac{RT}{F} \ln \frac{a_{H^+,2}}{a_{H^+,1}}$$

and the activity $a_{H^+,1}$ could be determined from the observed electromotive force if $a_{H^+,2}$ is a standard for reference.

As a matter of fact, the situation is not so simple as this, because the glass membranes that are usually used, or at least those which have been described in the literature, are not symmetrical, *i.e.*, they do not have quite the same properties at the two surfaces. In practice, the resulting asymmetry potential has been determined by using solutions of known hydrogen-ion activity (buffer solutions whose pH value has been determined by using the hydrogen electrode), thereby calibrating the electrode. Various kinds of reference electrodes are used.

One of the difficulties in the use of the glass-electrode system is the extremely high internal resistance of the cell which results because of the inclusion of the glass diaphragm in the cell chain. Even the most sensitive galvanometer can hardly give a satisfactory response. The instruments for the measurement of cell potential most commonly used have been the quadrant electrometer and the vacuum-tube voltmeter. There are now available a number of compact and portable laboratory assemblies which are accurate, sensitive, and rapid in operation. In these instruments the vacuum-tube voltmeter is used.

The object of this experiment is to illustrate the operation of a commercial glass electrode apparatus by making a titration curve of a protein. It now seems well established that proteins can combine with hydrogen or hydroxyl ions. By the use of an electrode that measures hydrogen-ion concentration it is possible to obtain titration curves in protein solutions to which either acid or base is added. By subtracting the concentration of free hydrogen or hydroxyl ions from, the total concentration of the strong acid or base used, a value for the

amount of hydrogen or hydroxyl ions bound by the protein is obtained.*
The glass-electrode system is used in making the titrations, and in
order to compute ion concentrations from pH values it is necessary
to assume that hydrogen- and hydroxyl-ion activity coefficients in
solutions of different concentration do not vary from unity and are
unchanged in the presence of protein.

The amount of strong acid that is combined with a dissolved
protein may be calculated from electromotive-force measurements with
a concentration cell of the type

$$\text{H}_2, \text{ protein} + \text{HCl (c}_1)\|\text{HCl (c}_1), \text{ H}_2$$

The electromotive force of such a cell is given by the expression

$$E = \frac{RT}{F} \ln \frac{c_{\text{H}^+} \text{ (aqueous solution)}}{c_{\text{H}^+} \text{ (protein solution)}}$$

If there are g grams of protein per kilogram of water, and if 1 g of
protein binds x equivalents of hydrogen ion, this formula becomes

$$E = \frac{RT}{F} \ln \frac{}{c_1 - gx}$$

In the same way the protein solution may be titrated with alkali
by using the cell

$$\text{H}_2, \text{ NaOH (c}_2)\|\text{protein} + \text{NaOH (c}_2), \text{ H}_2$$
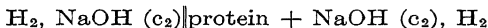
The electromotive force of this cell is

$$E = \frac{RT}{F} \ln \frac{c_{\text{H}^+} \text{ (protein solution)}}{c_{\text{H}^+} \text{ (aqueous solution)}} = \frac{RT}{F} \ln \frac{c_2}{c_2 - gy}$$

in which 1 g of protein is assumed to bind y equivalents of hydroxyl
ion, *i.e.*, it loses y equivalents of hydrogen ion.   As noted in Exp. 49
it is not practical to use two hydrogen electrodes.   For this experiment
a glass electrode–calomel system is recommended for the determina-
tions of the hydrogen-ion concentrations of the solutions containing
protein.

The titration curve is an accurate method of defining the acid
and base combining properties of a protein, but it will not contain

---

* Actually an electromotive-force measurement does not yield a hydrogen-ion
concentration.   By making certain assumptions such an observation yields hydro-
gen-ion activity, *i.e.*, hydrogen-ion concentration multiplied by an activity
coefficient.   The activity coefficient, a function of many variables, approaches unity
in very dilute solutions.

sharp breaks since it is a composite of a number of dissociation curves with overlapping constants. The behavior of a simple aminoacid such as glycine is in striking contrast. Actually the aminoacid has a salt-like nature in water solution, and the law of mass action for it is formulated in accordance with the assumption that the undissociated form is a dipole·ion (in German, Zwitter-ion). The reactions in acid and base are

$$^+NH_3\ CH_2\ COO^- + HCl \rightarrow\ ^+NH_3\ CH_2\ COOH + Cl^-$$

and

$$^+NH_3\ CH_2\ COO^- + NaOH \rightarrow NH_2\ CH_2\ COO^- + Na^+ + H_2O$$
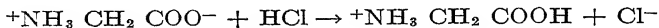
They may be followed by potentiometric titration.

Experimental support for the correctness of this description of the reactions in the presence of acid and of base has been given by Harris who titrated a number of the aminoacids and polypeptides in the presence of formaldehyde. This chemical reacts with $-NH_2$ groups but not with carboxyl groups, so that the modification in the titration curve in the presence of formaldehyde must be ascribed to the amino groups. When glycine is titrated with an acid it is the carboxyl group that is involved, and in the base titration only the amino group is concerned.

Apparatus.—Commercial glass electrode assembly; buffer solutions; 0.1N HCl and NaOH solutions; 1 per cent gelatine; glycine.

Procedure.—The glass electrode is shown in Fig. 43. The fragile glass electrode should be protected with a large vertical, open end glass tube having large holes in its sides. The tube is set firmly in position around the electrode with a sealing-wax joint at the top. A 100-ml portion of one per cent gelatine solution is titrated with 0.1N sodium hydroxide solution. The glass bulb and salt bridge of the glass electrode are placed in the solution, and the pH of the solution is measured at intervals as the alkali is added. The solution is agitated by a stirrer driven by an air motor. Great care is necessary in arranging the stirrer so that it cannot break the fragile glass electrode. The same process is repeated with another 100-ml portion of protein solution except that 0.1N hydrochloric acid is used in the place of the base.

Similar titrations are performed with 50-ml portions of 0.1N glycine, by adding 0.1N acid and 0.1N alkali. The acid and base titrations are repeated after the addition to the glycine solution of sufficient formaldehyde to make the solution 2 per cent in this reagent.

Calculations.—The data for the protein titration together with the results of the first computation are conveniently tabulated under the headings, Total Volume of the Solution, NaOH Added in Moles per Liter, pH of the Solution, pOH, Uncombined NaOH in Moles per Liter, Combined NaOH in Moles per Liter, and Combined NaOH per Gram of Protein. Data and figures to correspond are collected to form another table for the hydrochloric acid titration. The headings
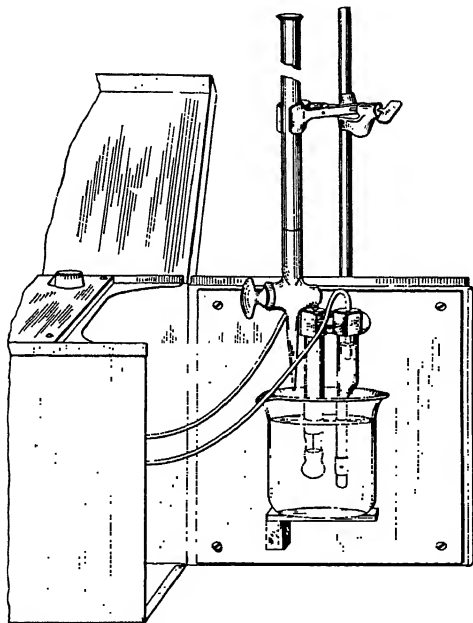

FIG. 43.—Glass electrode with electron-tube potentiometer.

of the several columns are Total Volume, Added HCl in Moles per Liter, pH of the Solution, Uncombined HCl in Moles per Liter, Combined HCl in Moles per Liter, and Combined HCl per Gram of Protein.

The complete titration curve is obtained by plotting moles of NaOH and HCl bound to 1 g of protein as abscissas against pH values of the solution as ordinates. The abscissas are laid out in such a way that the points of zero addition of acid and of base coincide, and bound acid and bound alkali per gram protein are plotted away from this zero point.

Titration curves are plotted for the acid and base titrations of glycine, without and with formaldehyde. To form the curves milliliters of added acid and base give the abscissas (again laid out in such a way that the points of zero addition of acid and base coincide), and the pH values of the solution determine the ordinates.

Practical Applications.—The combination of proteins with acids and bases is due to their dissociation as amphoteric electrolytes and the titration curve of a protein represents a summation of the individual dissociation curves with overlapping constants. Many investigators have attempted to analyze the titration curves of proteins in terms of the summation of the dissociation of univalent acids and bases. The combination of egg albumin with acid can be expressed by means of an equation of the form

$$pH = pK_A + \log \frac{(salt)}{(acid)}$$

At the point of half neutralization for solutions in acid

$$pH = pK_A = 3.5$$

In the corresponding way for solutions in alkali we have

$$pOH = pK_B + \log \frac{(salt)}{(base)}$$

At the point of half neutralization

$$pOH = pK_B = 10.5$$

These figures are to be verified and compared with the constants   and which are obtained from the glycine titration curves.

Constants describing the behavior of various proteins in relatively alkaline and acid solutions have nearly the same value. Ranges in which values fall are consistent with the notion that the reactive groups in the protein molecule are derived from the groups of amino acids of which proteins are composed.

Suggestions for Further Work.—The glass electrode may be used for the measurement of the pH of a wide variety of miscellaneous substances such for example as the following: milk, sour milk, blood, orange juice, lemon juice, water extract of soil, tap water, tap water from which carbon dioxide has been expelled. The carbonic acid, bicarbonate ion equilibrium, and the hydrolysis of various salts, may be calculated from measurements of pH.

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52. Hydrolysis by Electromotive-force Measurements

One of the applications of pH measurements is illustrated in this experiment, *viz.*, the quantitative determination of the extent to which a salt is hydrolyzed.

Theory.—When a salt undergoes hydrolysis, an undissociated base or acid is formed, leaving in the first case an excess of hydroxyl ions and in the latter an excess of hydrogen ions. The theory of hydrolysis has been discussed in Exp. 45, in which the extent of hydrolysis was determined by measurements of conductance of the solution. More generally and more accurately the extent of hydrolysis may be determined by determining the concentration of hydrogen ions in the solutions under conditions that do not disturb the equilibrium in the solution.

The hydrolysis of aniline hydrochloride $C_6N_5NH_2 \cdot HCl + HOH \rightarrow HCl + C_6H_5NH_2 \cdot HOH$ may be considered. The hydrochloric acid may be assumed to have undergone complete dissociation, and the aniline formed will be practically undissociated. If aniline hydrochloride is dissolved to a concentration of c gram equivalents per liter, and the degree of hydrolysis is x, then the activities of the products of the reaction will be xc. As the hydrochloric acid is completely dissociated, the product xc will also represent the activity of the hydrogen (and chlorine) ions. This hydrogen-ion activity is the quantity that is determined electrometrically. Writing the equilibrium constant K_h for the hydrolysis

$$\frac{x^2 c}{1 - \varepsilon} \tag{1}$$

The use of the hydrogen electrode for the determination of the hydrogen-ion activity is, of course, limited. The glass electrode makes possible a much wider application of the method, for it allows the determination of the hydrogen-ion activity in solutions of salts that would plate out on the hydrogen electrode or react with hydrogen and platinum.

Apparatus.—The apparatus necessary for this experiment is that described in Exp. 51; salt bridge; aniline hydrochloride; copper sulfate.

Procedure.—Solutions 0.02N, 0.01N, and 0.005N of aniline hydrochloride in conductance water are prepared. The hydrogen-ion

activities of these salt solutions are determined with the glass electrode (or the quinhydrone electrode).

The degree of hydrolysis of certain metallic salts, in solutions of known concentration, may also be determined. Solutions of any one of the following salts will illustrate the principle: nickel chloride, cobalt chloride, zinc chloride, ammonium chloride, nickel sulfate, cobalt sulfate, zinc sulfate. Conductance water should be used in preparing all the solutions.

As an example of a salt of a metal more noble than hydrogen, copper sulfate or cuprous chloride may be used. Solutions of these salts are made to definite concentrations, and the hydrogen-ion activities of the solutions are determined by means of the quinhydrone electrode.

For example, for $0.01N$ copper sulfate solution the hydrogen-ion activity is determined by an electromotive-force measurement on the cell

$$\text{Hg}|\text{Hg}_2\text{Cl}_2, \, N \text{ KCl}|N \text{ KCl}|\begin{matrix}0.01N \\ \text{CuSO}_4\end{matrix}| \qquad \text{Au}$$
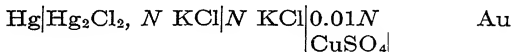
The hydrogen-ion activity is calculated from the formula for the quinhydrone electrode given in Exp. 49

$$E = 0.4185 - 0.0591 \log \frac{1}{a_{\text{H}^+}}$$

Calculations.—Since the activity of the hydrogen ion a_{H^+} is given by the expression xc, the degree of hydrolysis x is readily calculated for the various concentrations c.

The value of the hydrolytic constant K_h for each salt is calculated from the degrees of hydrolysis at the various concentrations by equation (1).

By assuming the ionic product constant for water to be 1×10^{-14}, the equilibrium or dissociation constant for the base may now be calculated (page 176).

Suggestions for Further Work.—The salts studied are of the type

$$\text{MA} + \text{HOH} \rightarrow \text{H}^+ + \text{A}^- + \text{MOH}$$
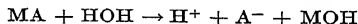
salts of a strong acid and weak base.

The method may also be applied to certain salts of the opposite type, for example, sodium acetate. For the determination, cells of the following type are used:

$$\text{H}_2 \text{ (1 atm.)} \begin{matrix}0.001N \\ \text{NaAc}\end{matrix}\begin{matrix}0.001N \\ \text{NaCl}\end{matrix}\begin{matrix}0.001N \\ \text{HCl}\end{matrix}\text{H}_2 \text{ (1 atm.)}$$
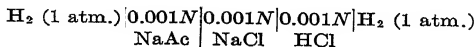
These cells are, in effect, hydrogen-ion activity cells, similar in all respects to cells of the type

$$H_2 \text{ (1 atm.)} | H^+ \| H^+ | H_2 \text{ (1 atm.)}$$
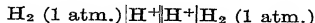
The activity of the hydrogen ions in the sodium acetate solution may be calculated from the observed electromotive force of the cell, on the assumption that the electrolytes, sodium chloride and hydrochloric acid, are completely dissociated.

References

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53. Free Energy and the Equilibrium Constant

This experiment illustrates the important relation between equilibrium constants and free energy and connects chemical and electrical measurements through thermodynamics. Practice is obtained in the use of the potentiometer, the volumetric analysis of silver and certain inorganic preparations.

Theory.—One of the most important equations of physical chemistry is that connecting the free-energy increase ΔF^0 with the equilibrium constant K

$$-\Delta F^0 = RT \ln K \tag{1}$$

This equation becomes exact if the equilibrium constant K is expressed in terms of activities, and it is useful as an approximate equation when K is expressed in moles per liter or in partial pressures.

The free-energy change involved in a chemical reaction may be obtained by addition and cancellation of several reactions, in the same way that heats of reaction are obtained from thermochemical equations. Tables of free energy are being accumulated, which will eventually permit a calculation of the equilibrium constant for most chemical reactions. It is possible also to calculate free energies from heats of reaction and entropy values, the latter being obtained from specific-heat measurements down to absolute zero.

When it is realized that an equilibrium constant enables one to calculate just how far the chemical reaction will go, the importance of these free-energy tables is apparent. Through these thermodynamical relationships, the concentration of products at equilibrium can be predicted when the concentration of the reacting materials is known. If the reaction is slow, considerations of reaction rate may, however, become more important than considerations of free energy and equilibrium.

The free-energy change in a chemical reaction may be determined most accurately and most directly by measuring the voltage of the reversible cell which represents the reaction.   The reaction

$$Fe^{++} + Ag^+ \rightleftarrows Ag + Fe^{+++} \tag{2}$$
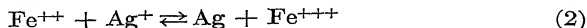
is particularly suitable for testing equation (1), because the equilibrium is quickly reached and easily obtained by volumetric analysis, and the free-energy change may be calculated directly from the voltage of the cell

$$Pt|Fe^{++}, \ Fe^{+++}\|Ag^+|Ag \tag{3}$$
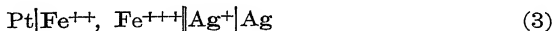
Apparatus.—Two bottles (150 ml); platinum electrode; silver electrode; two half-cells; calomel cell; potentiometer; galvanometer; standard cell; 50-ml pipette; burette; $0.2M$ ferric nitrate; $0.4M$ ferrous sulfate, $0.4M$ barium nitrate; $0.1M$ nitric acid, $0.1M$ silver nitrate, $0.1M$ potassium thiocyanate, carbon dioxide.

The principle of the potentiometer and the wiring diagram (pages 189 and 371) should be fully understood.

Procedure.—About 3 g of precipitated silver is added to 50 ml of $0.200M$ ferric nitrate and mixed with 50 ml of $0.1M$ nitric acid in a flask or bottle.   The air is thoroughly swept out with carbon dioxide, and the bottle is stoppered and greased.   Oxidation of ferrous ions by air constitutes one of the greatest difficulties in this experiment.

A second bottle is prepared in the same way, and the two are heated to about 50°.   They are removed and shaken at frequent intervals and allowed to stand several hours.   The nitric acid prevents hydrolysis.

If the finely powdered metallic silver is not available, it is prepared by dissolving about 10 g of silver nitrate in water and adding it to an excess of ferrous sulfate solution.   The precipitate of silver is filtered and rinsed with hot distilled water until the rinsings give no test with the potassium thiocyanate.

The electrical measurements are made while the silver and ferric nitrate solution is set aside to reach equilibrium.   Ten milliliters of $0.200M$ ferric nitrate is mixed with 10 ml of $0.200M$ ferrous nitrate, and the resulting solution is then mixed with 20 ml of $0.1M$ nitric acid. The ferrous nitrate is prepared just before using by mixing equal portions of $0.400M$ ferrous sulfate and barium nitrate that is very slightly more concentrated than $0.4M$.*   The barium sulfate precipitate is allowed to settle, and the clear filtrate of ferrous nitrate is poured off.   A drop of barium nitrate should give no precipitate when added to the filtrate.   A platinum electrode is inserted in this solution, and the potential is measured against a normal calomel electrode, using a

* The solution is warmed to help dissolve the barium nitrate.

bridge of saturated ammonium nitrate. Apparatus for the determination of electrode potentials is described in Exps. 48 and 49.

A silver electrode is inserted in the $0.1M$ silver nitrate, and the potential is measured against a normal calomel electrode, using a bridge of saturated ammonium nitrate. The silver electrode is best prepared by depositing a spongy mass of silver on a platinum wire, electrolyzing in silver cyanide solution at high current density, followed by rinsing with the $0.1M$ silver nitrate solution which is to be studied.

The two potentials may be checked by eliminating the calomel cell and measuring directly the potential of the ferrous-ferric electrode against the silver electrode.

The solutions of metallic silver and ferric nitrate which have been standing to come to equilibrium are analyzed for silver ions, and it is assumed that the concentration of ferrous iron is equal to that of the silver. A 25-ml sample of the solution is titrated with $0.1M$ potassium thiocyanate, the ferric nitrate already in solution serving as an indicator. The potassium thiocyanate solution is standardized with the silver nitrate solution, an equal volume of the ferric nitrate solution being added as a comparable indicator.

The titrations should be made as soon as the stoppers are removed, in order to avoid air oxidation.

Calculations.—The fundamental equation is

$$E = \frac{RT}{nF} \qquad \frac{RT}{nF} \qquad \frac{a^x \text{ products}}{a^y \text{ reactants}}$$

in which products are defined as the materials at the right of the equality sign and reactants as the materials at the left, and x and y refer to the stoichiometrical proportions 1, 2, 3, etc., in which they occur. When the activities a are unity, the potential is defined as E^0, and then $E^0 = \dfrac{RT}{nF} \ln K$.

The concentration of silver ion in the equilibrium solution is calculated from the potassium thiocyanate titration. The concentration of the ferrous iron is the same as that of the silver, and the concentration of ferric iron is calculated by subtracting the ferrous iron from the ferric iron originally present. The equilibrium constant K is calculated as follows:

$$K = \frac{a}{}$$

The concentration of silver atoms does not appear in the calculation, because it is kept constant by the presence of the solid silver. The

electrochemical reactions at the two electrodes corresponding to the
cell given by equation (3) are

and

$$Ag^+ + e \rightarrow Ag$$
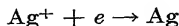
These are the reactions that cause electrons to move from right
to left within the cell as written.

The voltage $E^0{}_{Fe^{+++},Fe^{++},Pt,}$ corresponding to a solution in which
both ferric and ferrous ions are present at equal activities, is calculated
from the cell

$$H_2, \ H^+{}_{(a=1)} \| Fe^{++}, \ Fe^{+++}, \ Pt$$
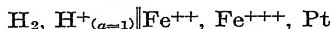
and from the equation

$$E^0{}_{Fe^{++},Fe^{+++},Pt} = E_{Fe^{++},Fe^{+++},Pt} - 0.0591 \ \log \frac{a_{Fe^{+++}}}{a_{Fe^{++}}}$$

where E is the measured voltage referred to the standard hydrogen
electrode. The E^0 value is calculated on the assumption that the
concentrations represent approximately the activities a. The value
of E^0 may be compared with that found in tables.

In practice the standard hydrogen electrode is replaced by the
normal calomel electrode, and 0.2805 volt is added to the observed
voltage.

The potential $E^0{}_{Ag^+,Ag}$, corresponding to the potential of a silver
electrode placed in a solution having an effective concentration of 1 eq.
of silver ion per 1,000 g of solvent, is calculated at 25° from the cell

$$H_2, \ H^+{}_{(a=1)} \| Ag^+, \ Ag$$
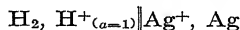
and the equation

$$E^0{}_{Ag^+,Ag} = E_A \qquad - \frac{RT}{nF} \ln a_{Ag^+} = \qquad - 0.0591 \ \log a_{Ag^+}$$

where $E_{Ag^+,Ag}$ is the observed potential, referred to the hydrogen
electrode as zero. The activity of the silver ion a_{Ag^+} is obtained by
multiplying the concentration $(0.1M)$ by the activity coefficient
(page 190). The value of $E^0{}_{Ag^+,Ag}$ may be compared with values found
in tables.

Then for the whole cell

$$= 0.0591 \ \log \qquad\qquad = 0.0591 \ \log K$$

The conventions having to do with the signs of single electrode potentials are given in Exp. 48.

The value of K is calculated from this equation and compared with the value of K obtained by direct analysis. The agreement can be only approximate, because analytically determined concentrations, rather than activities, are used for calculating K from the equilibrium mixture and for determining $E^0_{Fe^{+++},Fe^{++}}$, but since the solutions are fairly dilute and the extent of ionization of ferrous and ferric nitrate is similar, the error is not great. The contact potential between the unlike solutions is another source of considerable error.

Practical Applications.—Any chemical equilibrium can be calculated when the free-energy change is known. In accumulating tables of free energies for this purpose, the direct electromotive-force measurement of reversible cells constitutes one of the most valuable methods. The equilibrium between various oxidizing and reducing agents may be calculated from the oxidation-reduction potentials.

Suggestions for Further Work.—The results may be made considerably more accurate by carrying out the measurements with a series of more dilute solutions and extrapolating the value of log K and of E^0 to infinite dilution. At infinite dilution, the concentrations and activities become identical. More accurate determination of ferric iron is advisable, using reduction with zinc and titration with potassium permanganate. Better results are obtained with perchlorates instead of nitrates.

The oxidation of hydroquinone by silver ion is an excellent reaction[4] to study because the equilibrium can be determined accurately by iodiometric titration and dissolved oxygen from the air does not affect the results. The reaction is
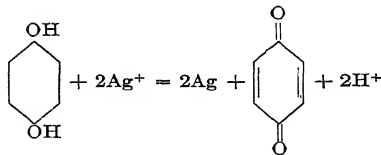
and the cell by which the equilibrium constant can be calculated is

Pt|quinhydrone (s), HNO_3 (0.1)M|HNO_3 (0.1M)|HNO_3 (0.1M) $AgNO_3$ (0.001M)|Ag

The voltage of the cell is easily measured, and the liquid junction potential is very small.

Various other equilibria may be calculated from electromotive-force measurements. The equilibrium $KSCN + TlCl \rightleftharpoons KCl + TlSCN$ has been studied in this way by Knüpffer.[5]

The dissociation pressure of copper oxide or mercuric oxide may be calculated from electromotive-force measurements of suitable cells.

References

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54. Electromotive-force Cells without Transference

For exact thermodynamical calculations the cells with transference are unsatisfactory on account of the uncertain liquid junction potentials. In this experiment it is shown how measurements can be made without these difficulties, using only cells in which there is no contact between unlike solutions.

Theory.—In previous experiments, there have been described electromotive-force cells with transference. A second kind of cell, characterized by effective identity in composition of electrolyte in both anode and cathode regions, is known as a "cell without transference." As a result of the effective identity in composition of anode and cathode solutions, migrations do not result in free-energy changes, and thus cannot be involved in the expressions for the electromotive forces. Cells of this second type are interesting on account of their theoretical significance. Their chief use is found in the determination of the activity coefficients of electrolytes.

As an example of a cell without transference we may consider the cell

$$H_2 \text{ (1 atm.)} | HCl (c_1), AgCl | Ag$$

The hydrogen electrode is reversible to hydrogen ions, and the silver chloride–silver electrode is reversible to chloride ions. The combination of this cell with another like it, except for the concentration of the hydrochloric acid, might be effected without forming a liquid junction, according to the scheme

$$H_2 \text{ (1 atm.)} | HCl (c_1), AgCl | Ag + Ag | AgCl, HCl (c_2) | H_2 \text{ (1 atm.)}$$

When negative current passes from right to left through such a double cell, one mole each of H^+ and Cl^-, and therefore one mole of hydrochloric acid, is removed for each faraday from the cell at the right and produced in the cell at the left. Since the results of the electrode processes are equal and opposite in the two halves of the cell, the free-energy change is due only to the transfer of hydrochloric acid from one side of the cell to the other, and the electromotive force of the combination is approximately

or exactly

$$a_{e_n} \tag{1}$$

The activities a_{e_1} and a_{e_2} pertain to the electrolytes and not to the ions.

Apparatus.—Potentiometer; galvanometer key; standard cell; dry cells; electrode vessels; hydrogen electrodes; mercurous sulfate electrodes; sulfuric acid solutions.

Procedure.—Since the silver chloride–silver electrode is somewhat inconvenient for general laboratory use, a similar cell making use of hydrogen and mercurous sulfate–mercury electrodes is suggested for the experimental work. The cell may be represented as follows:

$$H_2 \text{ (1 atm.)} | H_2SO_4, \ Hg_2SO_4 | Hg$$
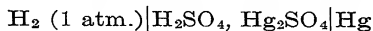
Owing to the fact that the solubility of the mercurous sulfate becomes appreciable at molalities of sulfuric acid 0.005 and below, cells using sulfuric acid at molalities 0.01, 0.05, 0.1, and 0.5 are best for the experiment. The voltages of these cells are determined so that the activity coefficients of the electrolyte may be calculated.

The hydrogen electrode consists of a piece of platinum wire or foil, the surface of which is coated with finely divided platinum and saturated with gaseous hydrogen as described in Exp. 49. The mercurous sulfate–mercury electrode is prepared from pure mercury, pure mercurous sulfate, and the sulfuric acid solution with which it is to be used. The electrode vessel should be of such form that the sulfuric acid does not come into contact with the platinum lead wire. Detailed directions for the preparation of these electrodes are given on pages 373 and 374.

The potentiometer with which the cells are measured is described on pages 189 and 371.

Calculations.—Since sulfuric acid is an electrolyte of unsymmetrical valence type, the working equation will be somewhat more complicated than the one derived for the symmetrical electrolyte hydrochloric acid. Lewis and Randall have shown that the electromotive force of such a cell is given by the expression

$$E = E^0 - \frac{RT}{2F} \ln a_e \tag{2}$$

where E^0, a constant, is the electromotive force of the cell in the standard state (*i.e.*, when the activity of the electrolyte is unity), and a_e is the activity of the electrolyte. Remembering that sulfuric acid is an

electrolyte of valence type 1–2, this equation may be reduced to one of the form

$$E = E^0 - \frac{RT}{2F} \ln \qquad\qquad \ln k\gamma m \qquad (3)$$

According to this equation, each electromotive-force measurement gives a quantity that is proportional to the activity coefficient γ. The constant k, which is seen to include E^0, must be determined from an independent measurement of the activity coefficient of the acid at some definite molality, because the ordinary methods of determination of E^0 by extrapolation to infinite dilution fail, owing to the solubility of mercurous sulfate. The constant k has been assigned the value 1.578×10^{-7}, using the data $\gamma = 0.397$ at molality $m = 0.05$, at the temperature $25°$.

Practical Applications.—Cells of this type make possible the determination of the activity of an electrolyte as a function of concentration, since the only free-energy change involved is a transfer of electrolyte from one concentration to another. It is readily possible to obtain the ratio between the activities of an electrolyte at any two concentrations; but, in order to make available the absolute value at any one concentration, the activity in a reference state must be known. The standard reference state is not any real solution; rather, it is an infinitely dilute one, in which the activity is unity. Since it is not always possible to make the extrapolation to infinite dilution, the method outlined in the previous section offers a practical solution of the difficulty.

Ratios of the electromotive force of a cell with transference to that of a double cell without transference give transference numbers provided, of course, the same two concentrations of electrolyte are used in each case.

Suggestions for Further Work.—LaMer and Parks[4] have reported electromotive-force measurements for the cell

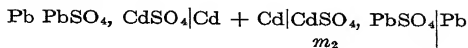Cd (two-phase amalgam)|CdSO$_4$, PbSO$_4$ (solid)|Pb (two-phase amalgam)
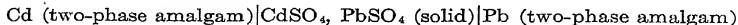
The lead sulfate–lead electrode is used in place of the mercurous sulfate–mercury one, because the appreciably lower solubility of lead sulfate permits accurate electromotive-force measurements to be made at lower concentrations. Cadmium amalgam electrodes are convenient to work with. From the electromotive forces of the cells using cadmium sulfate solutions at two concentrations, the free energy of transfer of a mole of the salt from one concentration to the other can be calculated. The electromotive-force equation is

$$(4)$$

The free-energy change involved in the transfer of a mole of salt from m_1 to m_2 is

$$-\Delta F = \frac{2 \times E \times 96{,}500}{4.185} \quad \text{cal.} \qquad (5)$$

The voltage E is that of the cell

$$\text{Pb} \; \text{PbSO}_4, \; \text{CdSO}_4 | \text{Cd} + \text{Cd} | \text{CdSO}_4, \; \text{PbSO}_4 | \text{Pb}$$
$$m_2$$

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55. Activity of Electrolytes and the Determination of the Standard Electrode Potential E^0

The standard electrode potentials E^0 are often used without full realization of the manner in which they are obtained. In this experiment one of the simpler of these potentials is determined by direct measurements and the usual extrapolation to infinitely dilute solutions. A high degree of accuracy is needed in the experimental measurements.

Theory.—The activity coefficient γ of an electrolyte is defined in such a way that it becomes unity at infinite dilution. At first sight it would appear easy to determine the electrode potential in a very dilute solution where the activity could be taken as equal to the concentration. However, the experimental determinations are very inaccurate in solutions of great dilution, and it becomes necessary to make accurate measurements in moderately dilute solutions and extrapolate to the very dilute ones. Even the extrapolation becomes uncertain unless some function of the measured concentration or electrode potential can be found that will give a straight line when graphed. Fortunately, there is theoretical backing for the straight line produced by plotting the potential of the electrode E against the square root of the ionic strength μ.

Once having obtained the correct value for E^0 in a solution where γ is unity, the activity coefficient of the electrolyte is easily calculated for any solution in which both the concentration and the measured electrode potentials are known.

Apparatus.—Potentiometer, preferably with a multiplying switch for giving greater sensitivity over a small range of low voltages; standard cell; wall-type galvanometer or other galvanometer of fairly high sensitivity; two silver electrodes; salt bridge of $2M$ NH_4NO_3 solution with agar plug; calomel electrode; exactly $0.1M$ silver nitrate; electrode cell; 25-ml volumetric flask; 100-ml volumetric flask.

Procedure.—The potentiometer is described on pages 189 and 371. The silver electrodes are prepared from strips of sheet silver with a narrow extension soldered to a copper wire and pulled through a glass

tube.   The end of the tube is then closed with melted sealing wax embedding the silver connecting strip.   The sealing-wax joint is then covered with melted paraffin which is more inert than the wax.   The electrode is cleaned by dipping in dilute nitric acid and giving it a thin coating of silver, by electroplating for a few minutes from a silver cyanide solution.   The electrodes are kept in distilled water away from contact with air.

The two electrodes are measured in $0.100m$ AgNO$_3$ solution against a standard calomel electrode.   The two should check within 0.1 millivolt.   The electrode is inserted through the rubber stopper of a cell provided with a side arm that dips into the ammonium nitrate solution.   An agar plug is used in the side arm to prevent diffusion. The agar plug is formed by drawing a warm solution of 10 per cent agar in $2M$ NH$_4$NO$_3$ into the connecting tube and allowing it to cool.

In this experiment the voltage measurements must be made with high accuracy, and the resistance of the cell is kept as low as possible in order to give large deflections of the galvanometer.   In accurate work it is necessary to exclude oxygen from most of the solutions in which the electrodes are immersed.   Accordingly, hydrogen or nitrogen is bubbled through the silver nitrate solutions just before introducing the electrode, and the cell is filled full so as to eliminate any air pocket.   Before inserting the electrode, it is rinsed with the same solution with which the cell is filled.

If the room temperature is not constant, it will be necessary to place the two electrodes in a thermostat or in beakers of water that are within a degree of the same temperature.

After checking the two electrodes against the calomel electrode, one of them is kept in its cell with $0.1m$ AgNO$_3$ as a reference while the other is placed in solutions of greater and greater dilutions, and the two are connected through a bridge of ammonium nitrate.   In this way the voltages measured are so small that the "low range" on the potentiometer may be used, to obtain a greater accuracy.

Twenty-five milliliters of the stock solution of $0.1m$ AgNO$_3$ (1.6989 g of AgNO$_3$ in 100 g of distilled water) in a volumetric flask is poured into a 100-ml volumetric flask, rinsed, and brought to the 100-ml mark with distilled water and mixed.   Part of the diluted solution is placed in the electrode cell, and hydrogen is bubbled through to sweep out dissolved air.   After the electrode potential is measured against the electrode in the $0.1m$ solution, the cell is refilled with the same solution and a check reading is made on the voltage.

Twenty-five milliliters of this solution is diluted to quarter concentration as before, and the process is repeated.   In this way voltage

readings are made in solutions of 0.1, 0.025, 0.00625, 0.00156, 0.000391, and $0.0000977m$ in silver nitrate as measured against the $0.1m$ silver nitrate. Check determinations are made in each case and averaged. In case the two readings do not agree, a third filling may be made.

Calculations.—The potential of the silver electrode in $0.100m$ $AgNO_3$ is measured against the normal calomel electrode and referred to the hydrogen electrode by adding the quantity 0.2805 volt. The potential of the silver electrode against the diluted silver nitrate solution is calculated in terms of the potential E referred to the standard hydrogen electrode.

The standard electrode potential E^0 is given by the expression

$$E^0 = E - \frac{RT}{nF} \ln a = E - \frac{2.303RT}{F} \log m\gamma \tag{1}$$

where a is the activity, m is the molality, and γ is the activity coefficient. For these dilute solutions it may be assumed that the concentrations are given in molalities even though the dilutions are made on the basis of volume.

For the purpose of extrapolation γ is taken as unity and E_m^0 is defined as follows:

E_m^0 and the ionic strength μ are calculated for each molality. Then E_m^0 is plotted against $\sqrt{\mu}$ and the best straight line is drawn through the points, giving less weight to the very dilute solutions where the errors are magnified. This straight line is extrapolated, and the intercept where $\sqrt{\mu} = 0$ gives the value of the standard electrode potential. When $\sqrt{\mu} = 0$, the solution is at infinite dilution where γ

Having determined the potential E^0 of silver in solution at unit activity of silver ions, the activity coefficient γ is calculated at each molality, using equation (1).

Practical Applications.—The determination of activity coefficients makes possible the use of the fundamental electrochemical formulas with exactness. When the molalities are multiplied by the activity coefficients, the resulting activities can be used without approximation. Most of the standard electrode potentials and activity coefficients of electrolytes have been determined by extrapolation in a manner similar to that illustrated here.

Suggestions for Further Work.—Standard electrode potentials and activity coefficients may be determined for other metals and electrolytes. Amalgamated zinc electrodes may be used in zinc sulfate solutions as described here for silver.

Amalgamated cadmium in cadmium chloride and lead in lead chloride solutions are also suitable.

When using divalent or polyvalent ions the necessary changes must be made in formulas (1) and (2) for calculating a and μ.

The influence of other electrolytes on the activity and activity coefficient of silver ion may be determined.   The formation of complex ions permits an interesting study.   For example, by adding sodium cyanide solution to the silver nitrate solution the silver is tied up in a complex ion which gives at equilibrium a very much decreased concentration of silver ion.   The activity is calculated from the measured value of E and the calculated value of E^0.   The activity coefficient is then computed from the known value of the molality.

References

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56. Activity Coefficient of Electrolytes by Solubility Determinations*

The concept and use of activities is emphasized in this experiment on the influence of electrolytes on the solubility of luteo cobalt iodate.

Theory.—It is a problem of paramount importance for the study of electrolytes to discover the theoretical and experimental bases for the laws of the dependency of the activity coefficient of an electrolyte upon the nature and concentration of the solution.   The method of measuring solubilities in the study of activity coefficients combines great simplicity with a high degree of accuracy.   This method is especially satisfactory at relatively high dilutions, and it is in this concentration region that Debye and Hückel have been successful in making theoretical calculations of the activity coefficients.   In this experiment the procedure consists of the determination of the increase in solubility of very difficultly soluble salts by the addition of small amounts of foreign salts that do not interact chemically with the saturating salt.   Then,

$$-\log \gamma = \log \frac{S}{S_0} - \log \gamma_0$$

where γ = the activity coefficient of the saturating salt.

S_0 = its solubility in pure water.

S = its solubility in the salt solution.

$\log \gamma_0$ = an additive factor which represents the activity coefficient of the salt in pure water.

* Although electromotive-force measurements are not here involved, this experiment is included in this chapter because of the importance of activities in electromotive-force studies.

If desired this additive factor may be determined for the difficultly soluble salt by extrapolating to infinite dilution a plot of log S/S_0 against $\sqrt{u}$, the square root of the ionic strength.

In such a problem as this the principle of Lewis and Randall concerning the ionic strength is applicable. The ionic strength is defined as $\frac{1}{2} \Sigma m_i z_i^2$, where m is the molality and z is the valence of any and all ions present in the solution.

The results of the calculations of Debye and Hückel for the activity coefficient of a salt in a dilute solution are given by the equation

$$-ln\ \gamma =$$

in which ν = the number of ions formed by the dissociating molecule.
ϵ = the unit charge of an ion (4.80×10^{-10} e.s.u.).
D = the dielectric constant of the medium at temperature T.
k = the Boltzmann constant (1.37×10^{-16} erg).
T = the absolute temperature.

n_i = the number of ions of the ith kind per milliliter.
When we express the concentration as the ionic strength in moles per liter and insert the values for the several constants, the following simple limiting expression is obtained for the activity coefficient of the saturating salt in an aqueous solution at 25°C.

$$-\log \gamma = 0.50z_+z_- \sqrt{\mu}$$

Apparatus.—Large thermostat fitted with horizontal rotating shaft and brass clips; 125-ml glass bottles; saturating salt, luteo iodate; sodium chloride; pyrex glass distillation apparatus; standard acid $0.02N$; standard alkali, $0.02N$; calibrated 5 and 10 microburettes; quartz-tube ammonia-distillation apparatus; brown cresol purple indicator solution.

Procedure.—In the present experiment the solubility of the complex cobaltammine salt luteo cobalt iodate $[Co(NH_3)_6](IO_3)_3$ is to be measured in water and in five sodium chloride solutions (0.001, 0.002, 0.004, 0.006, 0.008M). The salt luteo iodate is prepared by treating a solution of luteo chloride with a solution of sodium or potassium iodate. The concentrations of these solutions are adjusted so that a crystalline precipitate is obtained. The precipitate is washed with water until freed of electrolytes and then with alcohol and dried.

All solubility measurements are made with a thermostat that has been adjusted to 25°. The bottles of 125-ml capacity are attached

with brass clips to a horizontal rotatable shaft, placed midway between the top and the bottom of the rectangular thermostat. The shaft is rotated at a speed such that an excess of salt, when placed in the bottle with the desired solvent, tumbles from one end of the bottle to the other. At the start of the experiment somewhat more than 100 ml of solvent and an excess of saturating salt are placed in each of six bottles which are then stoppered and sealed. The bottles are allowed to rotate for at least 2 hr. and preferably for as long as 24 hr.

After saturation of the solutions the bottles are removed from the rotator and the excess salt is allowed to settle out. Two samples of 50 ml volume are withdrawn with a pipette to which has been attached a loose cotton plug made up in a short length of rubber tubing. This filter assembly which slips on over the end of the pipette prevents contamination of the salt solution with solid phase. In any event, the tip of the pipette is kept well above the solid phase as the sample is withdrawn.

The solubility of the saturating salt in the several solutions is calculated from analyses for ammonia. Owing to the presence in the luteo iodate of six ammonia groups per molecule, it is possible to determine the solubility of the salt in moles per liter with a relatively high degree of accuracy by adding sodium hydroxide to the saturated solution and titrating the ammonia liberated on distillation. A vitreous quartz tube about 5 ft. in length and 1 in. in diameter which has been bent in inverted U form is used as condenser. A 300-ml pyrex flask is sealed to a pyrex Kjeldahl distilling head which, in turn, is sealed to a pyrex glass tube that fits snugly at the end of the quartz tube. Gooch rubber tubing is used to make this joint airtight. A sample of the solution is admitted through a $\frac{1}{2}$ in. diameter side arm provided with a ground-glass stopper.

The ammonia is passed through the quartz condenser and is absorbed in a known excess of standard hydrochloric acid. In the back titration with standard alkali, brom cresol purple is used as an indicator. The two calibrated microburettes are used in the ammonia determination.

Calculations.—The activity coefficients of luteo iodate in the several salt solutions are determined by means of the effect of the solvent salt in changing the solubility of the highly insoluble saturating salt. The solubility relations may be tabulated in columns to give the concentration of solvent salt in moles per liter, equilibrium concentration of saturating salt in moles per liter, total ionic strength of the solution, square root of the ionic strength, and logarithm of the solubility ratio S/S_0.

In addition the values of the logarithm of the solubility log S/S_0, obtained directly from the analytical data, are plotted as a function of the square root of the ionic strength, and the limiting slope of the resulting curve is obtained. For comparison, the value of the slope calculated by the limiting law of Debye and Hückel is

$$0.5z_+z_- = 0.5 \times 3 \times 1 = 1.5$$

Practical Applications.—Solubility studies have found important use in the study of electrolytes. They have aided in the establishment of the general ideal equations of Debye which have to do with interactions between ions and between ions and the neutral molecules. They have also served to demonstrate the fact that in dilute solutions the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength.

Suggestions for Further Work.—The experiments may be extended by using other solvent salts, both of the same and of other valence types. For this purpose 1-1 type salt KSCN and 2-1 type salt BaCl₂ are recommended. Luteo iodate is not a good saturating salt for experiments in which the dielectric constant of the solvent is lowered by the addition of alcohol. It is a salt of highly unsymmetrical valence type. Unfortunately complex cobalt ammonia salts more suitable for this purpose are not readily available.

References

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57. Thermodynamics of Electrochemical Cells

The electromotive force of the zinc-lead cell is measured at different temperatures, and the heat of the reaction is calculated with the help of the Gibbs-Helmholtz equation.

Theory.—The following reaction is studied:

$$\rightarrow Zn^{++} + Pb \tag{1}$$

The heat evolved may be measured directly in a calorimeter under conditions where no useful work is performed, or it may be calculated from electrical measurements. Since the measurement of electrical quantities is so precise, the latter method is actually more accurate than the direct calorimetric method.

Instead of placing zinc directly in a solution of lead ions and carrying out the reaction irreversibly, the same reaction may be brought

about reversibly by constructing an electrochemical cell as follows:

$$\text{Zn, Zn}^{++}\|\text{Pb}^{++}\text{, Pb} \tag{2}$$

When the zinc and lead electrodes are connected with a wire, electricity flows as the zinc is consumed. A motor in the circuit can be made to do useful work, and the maximum amount can be obtained (theoretically at least) by drawing a very small amount of current. At any time the motor can be operated as a dynamo to reverse the current and cause electrolysis, thus depositing zinc and putting lead into solution.

The electrical work done by the cell when it is operating reversibly (*i.e.*, when only a very small quantity of current is being drawn off) is the maximum work. Since no gases are evolved and there is no appreciable pressure-volume work, the maximum work done is also equal to the decrease in free energy $-\Delta F$. Instead of measuring this quantity with an electrical motor, it is much more accurate to measure the voltage with a potentiometer and a galvanometer that draws practically no current. Then

$$nFE \tag{3}$$

where E is the measured voltage, n is the valence, and F is the faraday, 96,500 coulombs.

In some cells, it is possible to obtain more electrical work than corresponds to the heat of reaction, because the cell tends to cool off in operating and absorbs heat from the surroundings and converts it into work. In other cells, the maximum work is less than the heat of reaction, because the cell heats up while it is operating, and this heat, which is given to the surroundings, is taken from the total chemical energy of the reaction and less is available for the performance of work. In still other cells, such as the zinc-copper cell, the heat evolved in the reaction and the maximum work that the cell can perform happen to be nearly equal to each other. In such a cell, very little temperature change is produced by the operation of the cell.

The difference between the maximum work and the total energy change is equal to the absolute temperature T multiplied by the temperature coefficient of work at constant volume, as given by the Gibbs-Helmholtz equation, which is obtained by combining the first and second laws of thermodynamics. At constant pressure this equation is written

$$\tag{4}$$

where ΔF, ΔH, and ΔS represent, respectively, the change in free energy, heat content, and entropy. The free-energy change is obtained directly from the voltage E of the cell as given in equation (3). Then

$$nFE = -\Delta H + nFT \frac{dE}{dT} \tag{5}$$

The equation is subjected to experimental test in this experiment. The voltage and temperature coefficient of voltage are determined, and the value of ΔH obtained in this way is compared with the heat of reaction from tables as determined with a calorimeter.

If the cell is placed in a calorimeter while it is operating reversibly, the heat absorbed by the calorimeter divided by the absolute temperature will give a direct measure of the entropy increase ΔS. This quantity is quite different from the heat of reaction obtained by operating the cell irreversibly, as described, where no external work is done and all the energy of the reaction is converted into heat.

This experiment should not be attempted unless the potentials can be measured to 0.1 millivolt.

Apparatus.—Half-cells, with electrodes of zinc, and lead; $0.02M$ solutions of zinc sulfate and lead nitrate; salt bridge of $2N$ ammonium nitrate in agar; large beaker and effective stirrer; potentiometer, galvanometer, and standard cell; thermometer; mercury.

Procedure.—A galvanic cell is made as follows:

Zn (solid, saturated with Hg), $+$Zn$(NO_3)_2$ $(0.02M)$|
Pb$(NO_3)_2$ $(0.02M)$, Pb (solid, saturated with Hg)
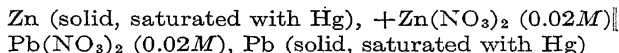
with two cut-off test tubes connected with a salt bridge of $2N$ NH$_4$NO$_3$ in a concentrated agar gel. The cells are provided with two-holed rubber stoppers, and the electrodes and the bridge are fitted tightly so as to prevent any leaks. As shown in Fig. 44, the cells are immersed in a large beaker of water with a motor-driven stirrer (or effective hand stirrer) and thermometer. If the apparatus cannot be freed from electrical short circuits in the water, it may be necessary to use a bath of light oil. The tubes are supported in two holes bored in a piece of wood.

The electrodes consist of a little mercury in the bottom of each test tube, one containing 60 per cent lead and the other 60 per cent zinc. The amalgamated metals give more reproducible potentials. Connections are made with short platinum wires sealed through glass tubes and connected to copper-wire leads. The tubes extend well above the level of the liquid in the thermostat.

The voltage of the cell is taken at about 0, 10, 20, 30, and 40°, waiting in each case at least 10 min. for the cells to reach the constant temperature of the bath, as determined by an unchanging voltage.

It is necessary to keep the temperature constant by stirring and dipping in a test tube filled with ice, or by introducing electrical heat. To make sure that thermal equilibrium has been reached, it is well to make measurements after cooling down from a higher temperature
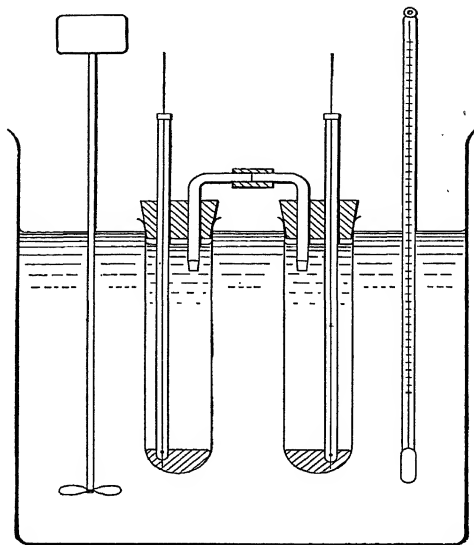

Fig. 44.—Electrochemical cell for determination of potentials at different temperatures.

to the required temperature, and again after heating from a lower temperature. The two should agree.

Calculations.—The voltage is plotted against the absolute temperature, and dE/dT is obtained by drawing a tangent to the curve.

The change in heat content ΔH is calculated from the voltage and the temperature coefficient of voltage, as given by the Gibbs-Helmholtz equation.

The change in heat content ΔH is compared with the maximum work nFE for each cell. Both quantities must be expressed in the same units, either in joules or in calories. The change in entropy ΔS is calculated.

Practical Applications.—The heats of reaction calculated by the Gibbs-Helmholtz equation are probably more accurate than those determined by calorimetry because electrical measurements are capable of much greater refinement than are thermal measurements.

The relation between ΔF and ΔH discussed in this experiment was carried down to low temperatures by Richards[1] and led to the first expression of what is now known as the third law of thermodynamics, "The entropy of a crystal at the absolute zero is zero."

Suggestions for Further Work.—Various other cells may be studied, including a copper-zinc cell in which ΔH and ΔF are nearly equal, a copper-lead cell, where ΔH is less than ΔF; and a silver-zinc cell, where ΔH is greater than ΔF.

The cell $Hg|Hg_2Cl_2|0.01N\ HCl|N\ KCl|N\ KNO_3|0.01N\ KOH + Hg_2O|Hg$ is also interesting.

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CHAPTER XII

ELECTRODE PHENOMENA

58. Transference Number of the Silver Ion by Use of the Silver Coulometer

The determination of the transference number of the silver ion by chemical analysis of the solution before and after electrolysis is a classical experiment. Since the transference number is close to 0.5 high accuracy is needed in the analytical procedure.

Theory.—Equivalent quantities of each ion involved in an electrolysis always separate at the cathode and anode. It does not follow, however, that each ion moves with the same velocity during the course of the electrolysis. Hittorf (1853) was the first investigator to obtain reliable information concerning the speed with which the ions move. He showed that, during electrolysis, concentration changes take place in the neighborhood of the electrodes, and that these changes are a measure of the ionic velocities. To be specific, the reduction in the number of equivalents of the cation in the anode section is proportional to the velocity of the cation, and the reduction in the number of equivalents of the anion in the cathode section is proportional to the velocity of the anion, provided these concentration changes are due to migration of the ions.

The transference numbers of the cation and anion are a measure of the fraction of the total current carried by them in an electrolysis. In terms of the concentration changes about the electrodes,

$$\frac{x}{x+y}$$
$$n_a = \frac{y}{x+y}$$

where n_c = the transference number of cation.

n_a = the transference number of anion.

x = the reduction in number of equivalents of cation in anode section due to migration.

y = the reduction in number of equivalents of anion in cathode section due to migration.

$x+y$ = the number of faradays of electricity passed during electrolysis.

The foregoing statements, as well as the principle of the experimental method, are illustrated by the following considerations: The vessel B (Fig. 45) is fitted with diaphragms XX' (real or imaginary) so that there are three compartments formed, an anode compartment about the anode An, a middle compartment, and a cathode compartment about the cathode Ca. If the vessel is filled with a solution of salt MA, the ions of which have velocities given by the ratio $M^+/A^- = \frac{3}{2}$, and if 1 faraday of electricity is passed through the solution, depositing one equivalent at each electrode, the following changes will be found to occur:

1. In Ca. One equivalent of M^+ is deposited from solution but $\frac{3}{5}M^+$ migrated in from the middle compartment. At the same time, $\frac{2}{5}A^-$ left this compartment and entered the middle compartment. Hence $\frac{2}{5}$ mole of MA is lost from Ca.
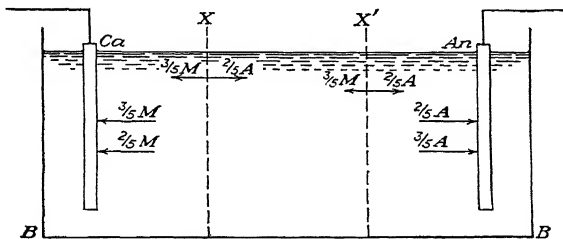
FIG. 45.—Theory of transference numbers.

2. In An. One equivalent of A^- is deposited from solution but migrated in from the middle compartment. At the same time, $\frac{3}{5}M^+$ left this compartment and entered middle compartment. Hence $\frac{3}{5}$ mole of MA is lost from An.

3. In XX'. It is evident from the diagram that there is no concentration change in this compartment. This is a necessary condition for all determinations of transference numbers.

In this situation, the decreases in salt concentration in the electrode compartments are in the ratio of the velocities of the ions moving away from the electrodes, making possible a calculation of the ratio.

Apparatus.—Transference number cell with silver electrodes; source of 90 to 110 volts d-c, milliammeter; stop watch; $0.05m$ silver nitrate; $0.05N$ potassium thiocyanate.

Procedure.—The apparatus is shown in Fig. 46. The transference numbers of the Ag^+ ion and of the NO_3^- ion are to be determined in this experiment. The vessel is filled with a 0.05 molal of silver

nitrate, the silver electrodes are put in place, and the cell is carefully leveled up and fixed in a rigid position.   It is then connected to a battery or rectifier such that a current of about 0.01 amp. will pass through the solution.   By means of a sliding-contact rheostat in series with the milliammeter and the source, the current may be adjusted to any predetermined value, preferably between 0.007 and 0.012 amp. Currents of greater magnitude should not be used, on account of the heating effect of the current, which might cause convection currents
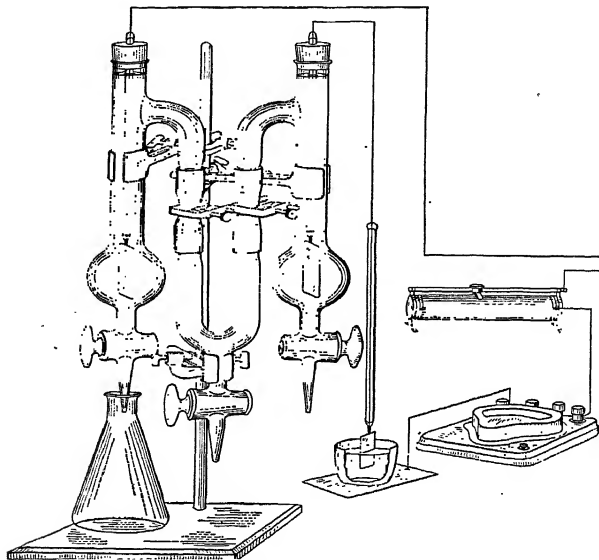
FIG. 46.—Cell for transference numbers with the silver coulometer.

to be set up.   The current is allowed to pass for a period of time between 90 and 150 min., accurately measured by means of a stop watch or electric clock.   The solutions in the anode compartment and cathode compartment are run into weighed flasks, after carefully closing off the central compartment with screw cocks.   The central compartment is then also drained into a flask and weighed.   The solutions are weighed, and the amount of silver in each is determined. This analysis is most readily carried out by titration with a standard potassium thiocyanate solution using ferric sulfate as indicator, in a solution made slightly acid with nitric acid.   Since the concentration changes in the electrode compartments are small, it is necessary that

these analyses be performed with utmost care. It is necessary, too, that the solution in the middle section shall have the same concentration as the original solution. The thiocyanate solution is standardized against a weighed quantity of silver nitrate or of silver.

The silver coulometer is described on page 376. It is filled with 15 per cent by weight of silver nitrate in water. The silver anode is wrapped in filter paper to prevent particles falling from the anode onto the cathode. The platinum crucible is cleaned with warm sulfuric acid and dichromate cleaning solution, rinsed thoroughly, heated at 110°, cooled in a desiccator, and weighed. The silver crystals deposited on the cathode will not stick unless the surface is clean.

The silver nitrate solution is poured back into a bottle, and the crucible is washed carefully with distilled water. Then it is heated in an oven at 110°, cooled in a desiccator, and weighed.

Calculations.—The calculation of the transference numbers of the ions follows directly from the analyses of the solutions in each of the electrode compartments before and after the experiment. The quantity of electricity in coulombs is obtained from the weight of silver deposited, 96,500 coulombs corresponding to 107.88 g of silver.

The number of equivalents of silver in the weighed quantity of electrolyte is determined in each of the three compartments. The change in the number of equivalents in the cathode compartment is the difference between the total number of equivalents in the weighed sample and the number of equivalents contained in an equal weight of water in the original solution as determined from the titration of the solution in the middle compartment. From this total change in concentration is subtracted the number of equivalents deposited in the coulometer because this number was deposited also from the cathode compartment onto the cathode.

After making this correction for the electrode reaction the change in the number of equivalents is the change due to migration. Dividing this number by the total number of equivalents deposited in the coulometer gives the transference number of the cation.

A check calculation is made for the transference number of the cation by using the titration values of the anode solution and of the solution in the middle compartment after allowing for the introduction of silver from the anode.

The transference number of the anion n_a is determined by subtracting the transference number of the cation n_c from unity.

The current passing is calculated from the coulometer and the time. The ammeter is calibrated by this means.

Practical Applications.—Transference numbers have an important application to the so-called electromotive-force cells with transference. In this type of cell,

there is a potential difference established at the surface of contact of the two solutions of different concentration which is difficult to measure and which can be avoided only with extreme care. This potential difference is due to a migration of the ions from the concentrated to the dilute solution, and it becomes zero only when the anion and cation have the same velocity. It is, however, possible to approximate the magnitude of this potential by certain formulas which have been proposed from time to time, and which always involve a knowledge of the magnitude of the transference numbers. For further details, References 1 to 4 may be consulted.

A less general application is the use of transference data to obtain information concerning the composition of ions. For example, if a solution of $KAg(CN)_2$ is electrolyzed, it is found that the concentration of the silver actually increases in the anode compartment, showing that the silver is contained in a complex negative ion.

Suggestions for Further Work.—There are several other methods for the determination of transference numbers which may be conveniently studied in the laboratory.

Transference numbers may be determined electrometrically with satisfactory results. The following cells are convenient for laboratory work:

I. H_2 (1 atm.)$|HCl$ $(a_1)|HCl$ $(a_2)|H_2$ (1 atm.)
II. H_2 (1 atm.)$|HCl$ (a_1), $AgCl|Ag + Ag|AgCl$, HCl $(a_2)|H_2$ (1 atm.)

Cell I involves transference whereas cell II does not.
The electromotive forces of these cells are

$$\text{I. } E_t \quad 2n_a \frac{RT}{F} \ln \frac{a_2}{a_1}$$

$$\text{II. } E = 2 \frac{RT}{F} \ln \frac{a_2}{a_1}$$

The transference number of the cation is obtained by division.

$$E_t$$

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59. Transference Number of Copper Ion by Use of the Iodine Coulometer

In this experiment the copper ion, which has a small transference number, is determined by titration with sodium thiosulfate, and the

same thiosulfate solution is used also for the iodine coulometer to determine the quantity of electricity passing through the cell.

Theory.—The theory is discussed under Exp. 58.

Apparatus.—Transference number cell with copper electrodes; 90-volt B battery or 110-volt d-c dynamo; milliameter; rheostat; switch; stop watch; burette; tubes and platinum-wire electrodes for iodine coulometer; 1 liter $0.05M$ $CuSO_4$; 1 liter $0.05M$ $Na_2S_2O_3$; 100 ml $0.5M$ KI.

Procedure.—The arrangement of apparatus is shown in Fig. 47. The transference number cell and iodine coulometer are arranged in

90 v. D-C   Milliammeter
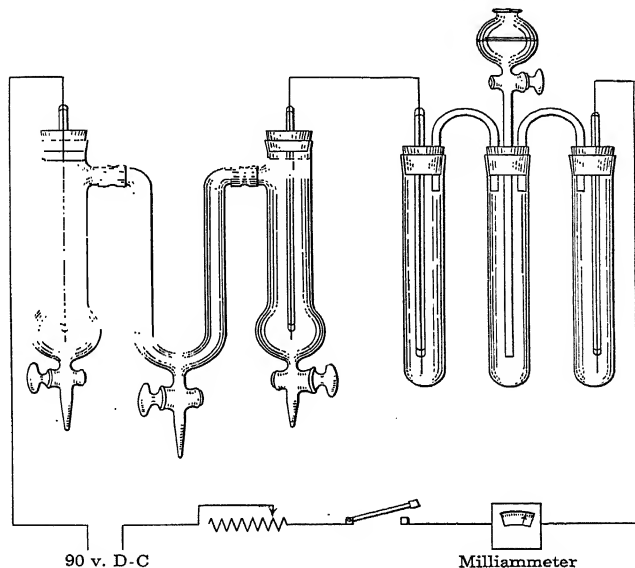
Fig. 47.—Cell for transference numbers with the copper coulometer.

position, and the rheostat is adjusted to maintain a constant current at about 10 milliamp. The current is passed for about an hour, and the time is taken with a stop watch in order to obtain an independent though accurate check on the coulometer. The transference cell is described on page 234. It is provided with copper electrodes and filled with $0.05M$ copper sulfate. In making the electrodes, No. 18 copper wire is slipped through glass tubing drawn down to give a snug fit and pieces of shellac or sealing wax are dropped in and melted at the bottom to close the tip.

The iodine coulometer has been developed to give accurate results by Washburn and Bates.[1] It consists of platinum electrodes in separate compartments containing $0.5M$ neutral potassium iodide. Each electrode consists of a coil of platinum wire protruding from a glass tube into which it is sealed. As fast as the iodine deposits on the anode from the passage of the current it is dissolved by the potassium iodide. This solution is drained off, *rinsed*, and titrated for iodine with $0.05M$ sodium thiosulfate, using soluble starch as an indicator. The connecting tubes and the cathode and anode compartments are filled by introducing the $0.5M$ potassium iodide solution through the central delivery tube which is provided with a stopcock. The stopper of the anode chamber is forced tightly into the nearly filled tubes, for any flow of liquid during the determination must be avoided. The stopper in the cathode chamber is provided with an open tube to permit escape of gas bubbles.

The solution in each of the three compartments is drained and tested for the total amount of copper by a standard procedure of analytical chemistry, titrating with $0.05M$ thiosulfate solution and using soluble starch as an indicator. Ammonium hydroxide is added drop by drop until the precipitate just clears, and then 5 ml of glacial acetic acid and 3 g of potassium iodide are added. The iodine liberated is titrated with thiosulfate. Each mole of iodine corresponds to 2 moles of copper. The thiosulfate is standardized with $K_2Cr_2O_7$, accurately weighed out, and added to a slight excess of acidified potassium iodide.

Calculations.—The transference numbers are calculated from the changes in copper concentration (Exp. 58). The data also permit a calibration of the ammeter.

Practical Applications.—These are discussed in Exp. 58.

Suggestions for Further Work.—These are discussed in Exp. 58.

<div align="center">References</div>

1. WASHBURN and BATES, *J. Am. Chem. Soc.*, **34**, 1341 (1912). Further references are given under Exp. 58.

<div align="center">

60. Transference Number of Hydrogen Ion by the Moving-boundary Method

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It is possible to determine transference numbers accurately by measuring the velocity with which the boundary between two solutions moves under measured electrical conditions.

Theory.—This method of procedure has some important advantages in that the actual ion migration may be observed, electrode and migration processes are differentiated, and precise results may be

obtained in a short time. It must be carefully noted that the velocity with which the boundary moves is not the same as the velocity of the ion in the solution on one side of the boundary unless the electrolyte furnishing the ion is completely ionized.

If c equivalents of electrolyte are dissolved in 1 liter of solution, $1{,}000/c$ is the volume in milliliters containing one equivalent. When 1 faraday of electricity F passes through the solution, the cation sweeps through a volume $n_c1{,}000/c$. If f coulombs are passed through the solution, the cation sweeps out V_c milliliters. Thus,

$$\frac{f}{F} = \frac{V_c c}{n_c 1{,}000}$$

During the course of an experiment the current i passing through the solution is kept constant, so that the number of coulombs f is equal to the time t in seconds multiplied by the current, and

$$n_c = \frac{V_c F c}{}$$

One faraday F is equivalent to 96,500 coulombs.

Apparatus.—Glass assembly shown in Fig. 48 fitted with cadmium and silver electrodes; d-c voltage source with rheostat; milliammeter; $0.1N$ HCl solution; indicator.

Procedure.—Before the apparatus is assembled, the volumes between the marks on the tube are found by a calibration with mercury. The glass portion is then cleaned with distilled water and rinsed several times with the $0.1N$ hydrochloric acid solution. It is then filled with the $0.1N$ acid to which has been added an adequate amount of methyl violet indicator. This indicator is green in acid solution and purple when neutral, and it is this color change that permits the observation of the time rate of movement of the boundary. The indicator should be added to the acid just before the start of the experiment, otherwise the color will fade. Reference to the diagram will indicate how the apparatus is set up and the electrical connections are to be made. The current is started flowing as quickly as possible. The hydrochloric acid should not be long in contact with the cadmium before the current is started. This precaution prevents the solution of cadmium and its subsequent motion up the tube and into the hydrochloric acid to cause an error in the hydrogen-ion transference number. As soon as the current begins to flow, the solution will show a boundary just above the cadmium-electrode surface and the boundary will move upward.

The current is kept constant at 5 milliamp. by a continual adjustment of the rheostat. There are recorded the exact times when the boundary crosses the marks to sweep out definite volumes. In the regions of the tube near the cadmium electrode the movement of the hydrogen ion is retarded, and in the first interval its mobility and transference number are too low. The value calculated in this region may be ignored.

Calculations.—Values of the transference number of the hydrogen ion are calculated by means of the formula developed above. In the
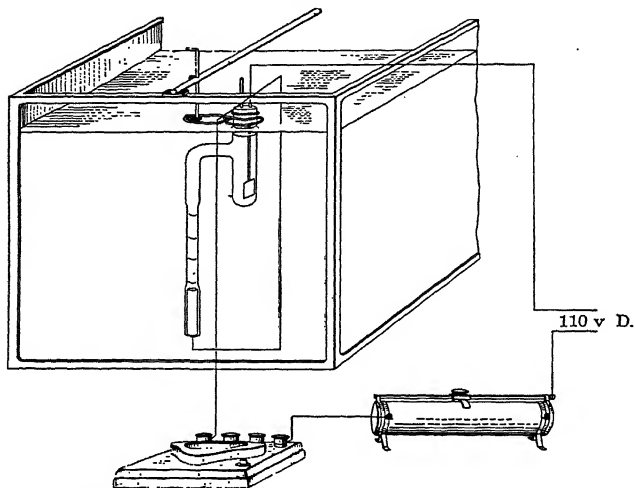
FIG. 48.—Moving boundary method for the determination of transference numbers.

formula, *c* now represents the concentration of the hydrochloric acid solution in equivalents per liter.

Practical Applications.—They have been discussed in connection with Exp. 58.

Suggestions for Further Work.—A few suggestions for additional work have been mentioned in Exp. 58.

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61. Decomposition Potentials. The Dropping Mercury Electrode

This experiment illustrates the determination and use of decomposition potentials. Through the determination of voltage–current curves and the magnitude of the current flowing, particularly with a dropping mercury electrode, it is possible to analyze qualitatively and quantitatively for most reducible or oxidizable solutes, whether inorganic or organic.

Theory.—The decomposition potential of a substance in solution may be defined as that potential which is just sufficient to cause continuous electrolysis to take place. This potential depends not only on the standard electrode potentials involved but also on the resistance of the solution and on surface effects. It may be visualized as that potential difference between cathode and solution which causes electrons to flow continuously from the cathode to the surrounding solute, or, in the case of the anode, the potential difference that causes a continuous transfer of electrons from the solute to the anode.

In the simplest method the applied electromotive force between two inert electrodes is gradually increased and its magnitude is measured with a potentiometer or voltmeter. A potential is readily found below which the current, as measured with a galvanometer or ammeter in series with the electrodes, drops steadily to a very small value on account of polarization and above which the current increases with the impressed electromotive force.

The use of the dropping mercury electrode in analytical chemistry is due largely to Heyrovsky who developed in Prague an accurate recording instrument with a sensitive galvanometer, which he called a "polarograph." It plots automatically on photographic paper the current as a function of the gradually increasing voltage, using freshly forming drops of mercury from a capillary tip as one electrode and a pool of mercury as the other.* The current curve rises as the voltage is increased, but there are flat sections of the curve which show the presence of reducible or oxidizable material in solution. Since the potentials at which these flat portions of the curve start are related to the decomposition potential and are characteristic of a given substance, they can be used for identification in qualitative analysis; and the magnitude of the current at these flat portions, the so-called "wave heights," are used for quantitative analysis. The method of analysis must be considered quite empirical, and the wave heights

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* Similar instruments are now made by several apparatus companies in this country.

must be calibrated with measured concentrations of the same material under the same conditions.

The use of the dropping mercury electrode for quantitative analytical purposes depends on the fact that solutes, whether electrolytes or nonelectrolytes, are reduced (or oxidized) when a current is passed through the solution at voltages above the decomposition potential. The current flowing then depends on the rate of diffusion of the material to the electrode, and this in turn depends on the concentration. The dropping mercury electrode gives reproducible results because a fresh surface of the electrode is being exposed continuously, but satisfactory results can be obtained also with an inert electrode of very small dimensions where the supply of electrons is concentrated over a small area. At low voltages a small current flows, and then as the voltage is increased above the decomposition potential, the current increases directly with the voltage in accordance with Ohm's law. As the voltage is increased still further, a point is reached after which the current is limited by the rate of diffusion of the reducible substance into the surface of the cathode. The current-voltage curve then becomes flat in the ideal case, and the current remains constant and independent of voltage until the voltage becomes high enough to produce some other chemical reaction at the cathode. If there are several different substances with nearly the same decomposition potentials, the resulting curve will be confused.

There are other complications which are discussed by Heyrovsky[2] and by Kolthoff.[3] A supporting electrolyte, about 0.1 mole of potassium chloride per liter, is added to minimize difficulties from the migration currents of ions. The adsorption of reducible substance on the surface of the mercury may cause a current to flow which is greater than the limiting current set by the diffusion rate. Maxima may then be produced in the curves which are not reproducible. They are eliminated in part at least by the addition of small amounts of adsorbable material such as carbohydrates, dyes, or ethyl cellulose, which are not reduced at the given potential.

Apparatus.—Dry battery (2 cells); rheostat (300 ohm); voltmeter (0 to 3 volts); galvanometer (10^{-7} amp. sensitivity is sufficient); variable resistance for galvanometer shunt (300 ohms); 5 cm capillary tubing (0.05 mm); platinum-wire electrodes; purified mercury; H_2SO_4; $NiSO_4$; $CdSO_4$; KCl; yeast; algae; acetophenone.

Procedure.—Voltage-current curves may be determined for the following: (1) sulfuric acid with platinum-wire electrodes; (2) sulfuric acid, cadmium, and nickel sulfates; (3) quantitative analysis for cadmium ion; (4) analysis for acetophenone in alcohol; (5) air, hydro-

gen, and oxygen with dropping mercury cathode; (6) analysis of oxygen content of yeast solution at different times; (7) analysis of oxygen content of suspension of green algae in dark and in light.

The assembled apparatus is shown in Fig. 49. The desired voltage from the two-cell dry battery is picked off on the rheostat of 300 ohms or more, and registered on the voltmeter. For the galvanometer, an inexpensive wall type with a 500-mm scale and a sensitivity of about 10^{-6} amp. is convenient. It should have a critical damping
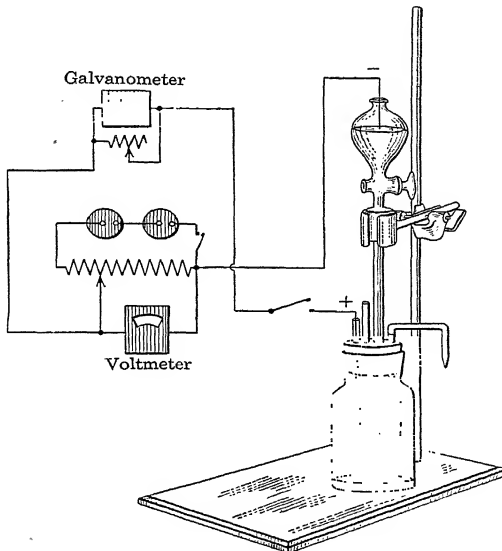
Fig. 49.—Dropping mercury electrode and circuit for decomposition potentials.

resistance in the neighborhood of 300 ohms, and the variable resistance of 300 ohms or more is used to prevent the galvanometer from going beyond the scale, and yet permit full utilization of the scale under different conditions. Both rheostats may be of the inexpensive radio type. The dropping mercury electrode has a resistance of many thousand ohms.

Before using the dropping mercury electrode a determination of the decomposition potential of dilute sulfuric acid $(0.01N)$ is made with ordinary platinum electrodes. The galvanometer shunt is adjusted to give a suitable deflection at about 2 volts, and the voltage is then

dropped nearly to zero and the corresponding reading of the galvanometer recorded. Successive readings are plotted as the voltage is increased a tenth or a few tenths at a time up to about 2 volts.

The capillary tip has a bore of 0.05 mm* and is about 5 or 10 cm long. The height of the mercury column is adjusted so that a drop falls every two or three seconds. A height of about 50 cm is usually convenient for this dropping rate. Purified mercury (page 444) is used, and the connecting tube of pure gum rubber is boiled with concentrated sodium hydroxide and thoroughly rinsed to remove sulfur compounds. If this 0.05-mm bore tubing is not available, small capillary tubing or a broken thermometer tube can be drawn down and cut off so as to give the proper rate of dropping. The galvanometer deflections pulsate with the dropping of the mercury, but the maximum deflections are recorded.

With the dropping mercury cathode a current-voltage curve is determined for a solution containing 0.001 g equivalent per liter each of $CdSO_4$, $NiSO_4$ and H_2SO_4. These electrolytes are added to a solution of $0.1N$ KCl. The small bottle is arranged as shown in Fig. 49. It is filled with the solution to be tested, and the dissolved air is bubbled out with hydrogen through the tube before the voltage current curve is determined. Dissolved oxygen is reduced at the cathode, and it affects the wave heights of some of the other solutes, hence it should be removed.

The wave height (the galvanometer deflections where the deflection is independent of voltage) is determined for 0.001, 0.0005, 0.00025 and $0.000125N$ $CdSO_4$ (each in $0.1N$ KCl solution) and plotted against concentration, sweeping out the oxygen each time. This calibration curve is then used for estimating the concentration of cadmium in an unknown solution.

It is possible also to determine certain organic compounds with the dropping mercury electrode. A current-volt curve is plotted for about 0.01 g of acetophenone dissolved in 100 milliliters of 50 per cent alcohol to which has been added about 4 g of sodium hydroxide. Readings are taken every 0.1 volt from 0.1 volt to 2.0 volts.

If dissolved air is not swept out, a level part of the voltage-current curve occurs at about 1 volt. This is the basis of a rapid method for the determination of dissolved oxygen,[4] an analysis that is useful in respiration studies and various biological investigations. It has been shown that if the galvanometer deflection at 0.1 volt is subtracted from the deflection at 1.0 volt, the difference is directly proportional

* Special fine-bore capillary may be purchased from the Corning Glass Works, Corning, N. Y.

to the concentration of dissolved oxygen. Most of the common reducible ions, which contribute to the current, affect the current also at 0.1 volt, and by taking the difference between the readings at 1.00 and 0.10 volt, their effects cancel out.

A solution of approximately $0.1N$ potassium chloride is allowed to stand for a few minutes with a piece of filter paper to provide a trace of adsorbable impurity, and air is then bubbled through for 2 or 3 min. Then a voltage-current curve, with readings taken every few tenths of a volt up to 1.5 volt, is determined with the dropping mercury cathode. The difference in deflection at 1.00 volt and 0.10 volt is recorded. Hydrogen is next swept through, and the voltage-current curve determined again. A third voltage-current curve is determined after bubbling oxygen through for a minute or two, and the deflections at 1.00 and 0.10 volt are recorded. The effect of dissolved oxygen on the wave height is evident from these measurements.

The apparatus is then used to follow the change in oxygen concentration during respiration. The cell is filled with a solution containing about 5 g of yeast, 1 g of sodium chloride, and 5 g of sugar in 100 ml of water, and the stopper is placed in tightly. The difference in galvanometer readings at 1.0 volt and 0.1 volt is determined every few minutes for a half hour or more, and these differences which are proportional to the oxygen concentrations are plotted against time.

If green algae are available, a thick suspension is placed in the tightly stoppered cell, and the consumption of oxygen by respiration is followed by taking the galvanometer readings at 1.0 volt and 0.1 volt at frequent intervals. A bright lamp is then placed near the cell, and the evolution of oxygen by photosynthesis can be followed by the increased galvanometer deflections. Readings are taken in successive periods of illumination and darkness.

Calculations.—The decomposition potential of sulfuric acid is obtained by plotting the galvanometer deflections against the impressed voltage obtained with the platinum wires. After passing the decomposition potential the current increases rapidly, and the extrapolation of this steep part of the curve back to the horizontal axis (zero current) gives the decomposition potential.

The wave heights are plotted against the known concentrations of copper so that by interpolation the concentration of an unknown solution of copper may be obtained from its wave height.

The voltage-current curves after bubbling through air, hydrogen, and oxygen show in a qualitative way the influence of dissolved oxygen on the wave heights. They may be used for a rough calibration of the oxygen concentration if desired. The concentration of oxygen in a

saturated solution in equilibrium with pure oxygen at atmospheric pressure is 0.0012 moles per liter, and the concentration with air is one-fifth as much.   If the galvanometer reading with pure oxygen at 1.00 volt is denoted by a and at 0.10 volt by b, whereas with a solution saturated with air the respective readings are denoted by c and d, then the concentration of oxygen in an unknown solution x having a 1.00-volt deflection of v and a 0.01-volt deflection of w is given approximately by the following formula:

$$x = \frac{(a - b) - (c -}{0.0012 - 0.00024} \; (v - w) \text{ moles per liter}$$

Accurate calibration requires the plotting of a curve of deflection differences for several concentrations of oxygen determined analytically.

The change of oxygen concentration with time for the experiments with yeast and with algae may be shown by simply plotting the difference in galvanometer readings at 1.00 volt and 0.10 volt against the time, or they may be estimated as shown in the preceding paragraph.

Practical Applications.—A knowledge of the decomposition potentials is important in calculating the energy requirements in an electrolytic process such as electroplating.

The dropping mercury electrode has found use in the analysis of a wide variety of substances such, for example, as most of the metals, acids, aldehydes, and ketones and many other organic materials, some of which are difficult to determine by other analytical methods.   The analyses can be made quickly and often with very small quantities of materials.   However, every analysis must be regarded as empirical, and reliable only when calibrated against known concentrations of the same material.

The dropping mercury electrode is useful in determining end points in certain titrations by plotting galvanometer deflections.[7]

Suggestions for Further Work.—Decomposition potentials may be determined for several different substances by plotting voltage-current curves with the platinum electrodes.   Lead sulfate, zinc sulfate, aluminum nitrate, and ferric chloride are suitable for such determinations.

The decomposition potential of hydrochloric acid may be measured at various concentrations $0.5N$, $0.25N$, $0.125N$ . . . $0.0078N$ obtained by successive dilutions.   The ratio of oxygen to chlorine liberated increases with the dilution.

The oxygen concentrations may be calculated accurately from the galvanometer readings by calibrating the particular dropping mercury electrode used in several solutions of known oxygen concentration, as determined by the Winckler method, using manganese sulfate and potassium iodide.*

Various factors may be studied in their influence on the respiration of yeast such as increased sugar content, addition of sodium cyanide or other poisons in small amounts, and irradiation with ultraviolet light.

* Directions for this procedure may be found in books on quantitative analysis; for example, TREADWELL and HALL, "Analytical Chemistry," vol. II, p. 650, 7th ed.; John Wiley & Sons, Inc., New York (1928).

In the study of photosynthesis by algae the influence of different variables may be investigated, such as the intensity of light and the additions of foods such as sugar and poisons such as dilute sodium cyanide. If a rectangular cell is used with a calibrated thermopile and a thick filter of $0.05N$ copper sulfate, the quantum efficiency of photosynthesis may be determined in absolute units.

The dropping mercury electrode may be used in the titration of lead salts as described by Kolthoff and Pan,[7] and in many other titrations.

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CHAPTER XIII

DIELECTRIC PROPERTIES

62. Dielectric Constant and Dipole Moment.   Capacity Determinations by Resonance Method

The simplest and, in many ways, the most satisfactory methods for the determination of a dielectric constant depend upon the measurement of the capacity of a condenser when empty and when filled with the material in question.   This capacity measurement may be made in a number of ways.   This experiment utilizes a resonance form of apparatus.

Theory.—Measurement of capacity involves the use of condensers. The meaning of the term "capacity" will be understood from the following consideration: Two conductors A and B are remote from other conductors and with a perfect dielectric between them.   Conductor B is grounded to keep it at zero potential, and conductor A is charged.   If Q is the charge necessary to bring the latter conductor to the potential V, the relation between these magnitudes is given by the equation

$$Q = CV$$

where C is the capacity of the body, and is a constant under any given set of conditions.

Where Q is given in coulombs and V in volts (practical units), the capacity C will be expressed in farads.   For practical purposes this unit is too large, and C is usually expressed in microfarads (μf). Small capacities are sometimes given in the still smaller units, the millimicrofarad (mμf) and the micromicrofarad ($\mu\mu$f).   The relation among the four quantities is expressed by the equation

$$1 \text{ f} = 10^6 \ \mu\text{f} = 10^9 \ \text{m}\mu\text{f} = 10^{12} \ \mu\mu\text{f}$$

The system of the two conductors A and B, previously described, constitutes a condenser.   The arrangement of the two conductors to form a condenser is accomplished in a number of ways in practice, resulting in the familiar forms such as the mica condenser, air condenser, and Leyden jar.   Condensers may be connected in parallel

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or in series as shown in Figs. 50 and 51, the combination acting as a single condenser.

The total capacity of a system of condensers connected in parallel is

$$C = C_1 + C_2 + C_3 + C_4$$

and the total capacity of the series arrangement of condensers is given by the expression

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} + \frac{1}{C_3}$$

or

$$C = \frac{1}{C_3}$$

In measurements of capacity, more particularly in connection with the measurement of dielectric constants, it is frequently necessary to resort to either or both of these groupings of condensers.

It is a well-known fact that the measurement of resistance in terms of the fundamental units of length, mass, and time involves considerable difficulty, but, having once established the resistance of a certain coil, other resistances may be readily and simply compared with it. Exactly the same thing is true with the measurement of capacity, for, given the
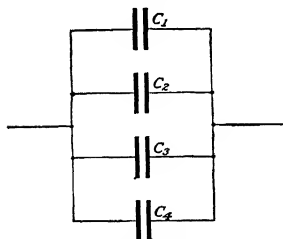
Fig. 50.—Condensers connected in parallel.
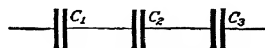
Fig. 51.—Condensers connected in series.

primary standards, the comparison of other condensers with these is accomplished with ease.

To return now to the consideration of the ideal condenser, we may assume the two conductors A and B to be parallel plates of equal area S, separated by a thin sheet of dielectric material of thickness d. The capacity of this condenser is very nearly proportional to the area of one of the plates and inversely proportional to the distance between them. In addition, it depends upon the nature of the dielectric material.

The formula for the capacity of such a condenser (parallel plate) can be shown to be

$$C = 0.0885$$

The proportionality constant ϵ depends upon the nature of the dielectric and is known as the "dielectric constant," or, less frequently, the "specific inductive capacity."

Since the dielectric constant of a vacuum is taken as unity, and that for air may be considered to be unity for practical purposes, the dielectric constant of any substance may be measured by comparing the capacity C_a of a condenser, in which air is the dielectric, with its capacity C_x, when the other substance forms the dielectric between the plates. This is expressed by the equation

$$\epsilon = \frac{C_x}{C_a}$$

It is evident from this equation that any method which serves to measure the capacity of a condenser will also serve to measure the dielectric constant of the condenser medium. The capacity of a given condenser is determined with air as a medium, and then with the substance in question as a medium. The ratio of the latter to the former gives the dielectric constant directly.

In recent years the polarization of molecules in an alternating electrical field has received much attention, both as a theoretical problem and as a subject for experimental researches. Originally, it was believed that the polarization was caused by a displacement of the charges within the molecule, such that one side of the molecule acquired a positive charge and the opposite side a negative charge of equal size. This pair of charges was considered as forming a dipole. Its dipole moment was the product of one charge multiplied by the distance between the charges. From such considerations as these, Clausius and Mosotti developed mathematical relationships which are now combined to give the so-called "Clausius-Mosotti equation," which follows:

$$P = \frac{\epsilon - 1}{\epsilon + 2} \; \frac{M}{d} = \text{constant}$$

In this expression, ϵ is the dielectric constant, M is the molecular weight, d is the density, and P is the molar polarization of the material in question. The formula proved to be valid only in the case of substances of low dielectric constant, or, as we know them now, nonpolar molecules. The polarizations of many other substances, called "polar molecules," varied with temperature, and therefore did not obey the Clausius-Mosotti equation.

In the case of these molecules of low dielectric constant, the molecular refraction obtained by the Lorenz-Lorentz formula (page 46),

was found to be approximately equal to the molar polarization, as would be expected from the electromagnetic theory of light. The situation with regard to molecules of higher dielectric constant remained obscure until Debye assumed that a molecule may contain a permanent electric or dipole moment of magnitude μ, as well as the induced moment mentioned above, both of which cause the molecule to become oriented in an electrical field and to contribute to the dielectric constant. This orientation of molecules is opposed by the thermal motions of the molecules; thus, the polarization becomes a function of the temperature. The Debye modification of the Clausius-Mosotti equation reads as follows:

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4\pi N}{3} \alpha + \frac{4\pi N}{3} \frac{\mu^2}{3kT} = P_d + P_0$$

Here N = the Avogadro number (6.02×10^{23}).

α = the polarizability or moment induced in a molecule by a field of unit strength.

k = the Boltzmann constant (1.38×10^{-16}).

T = the absolute temperature.

P_d = the polarization due to deformation or distortion of the molecule.

P_0 = the polarization due to orientation.

For nonpolar molecules, $\mu = 0$ and the second term of the right-hand side of the equation drops out; consequently, it becomes equivalent to the original Clausius-Mosotti expression. When the molecule is polar, *i.e.*, electrically unsymmetrical, its polarity is measured quantitatively by the magnitude of μ, and the polarization varies linearly with the reciprocal of the absolute temperature, according to the relation

$$P = a + \frac{b}{T}$$

where $a = \qquad \alpha$ and $b = \quad \overline{\vphantom{9k}\,9k\,}$

There are two general ways in which we may proceed to determine the dipole moment of a molecule. The first of these methods gives the more accurate result, but we shall use the second one, because the necessary operations are less time consuming.

1. When the dielectric constant ϵ and density d are measured over a range of temperature, the values of the quantities a and b may be evaluated from plots of molar polarization as a function of the recipro-

cal of the absolute temperature.   The value of the electric moment is obtained from the value of b.

2. The total molar polarization can be obtained from dielectric-constant and density measurements at a single temperature, and the polarization due to deformation can be approximated, using the Lorenz-Lorentz molar-refraction equation. The difference gives the molar polarization due to orientation, thus making possible the calculation of the electric moment.

Theoretically, the most suitable systems for application of the theory are gases at the lower pressures.   When the molecules are not free to orient, the Debye equation cannot be expected to apply.   Thus, in polar liquids, the electrical fields of the molecules are so close together that they restrict one another's freedom of motion.   However, when these molecules are dissolved to low concentrations in nonpolar solvents, relatively significant experiments can be made quite readily.   The molar polarization of a polar molecule dissolved in a nonpolar solvent may be calculated from the total polarization of the mixture and that of the pure solvent, assuming that the molar polarization of the latter is always proportional to its mole fraction in solution.   The polarization of the solute molecule corresponding to an infinitely dilute solution may then be obtained by extrapolation of the values obtained at the several finite concentrations.   The expression for the molar polarization of such a solution is

$$P_{1,2} = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{f_1 M_1 + f_2 M_2}{d} = f_1 P_1 + f_2 P_2$$

where $P_{1,2}$ = the molar polarization of the solution.
  f_1 and f_2 = the mole fractions of solvent and solute.
M_1 and M_2 = the molecular weights of solvent and solute.
  P_1 and P_2 = the molar polarizations of solvent and solute.
        d = the density of the solution at the temperature of the experiment.

Therefore, the determination of the electric moment of a molecule requires dielectric-constant and density data.   For laboratory purposes it is more convenient to work with solutions of the type just mentioned.   Their densities can be obtained by standard methods (page 321), but special types of apparatus are necessary for the dielectric-constant observations which are required.

Apparatus and Procedure.—In this experiment, the capacity measurements are to be made by a resonance method.   The disadvantage of this type of measurement is that it is not capable of an extremely high degree of accuracy.   On the other hand, it has the

tremendous advantage that it is particularly suitable for work with liquids having an appreciable electrical conductivity. Its operation may be described as follows: Suppose oscillations are generated in a circuit containing inductance and capacity; if a second circuit is brought into inductive relation with this first circuit, the condition of resonance will be indicated when the current or energy in the former reaches its maximum value. Under these circumstances, the inductance-capacity product of the two circuits will be equal. It is evident, then, that if the values of both inductances and one capacity are known, the value of the other capacity can be calculated from the condition for resonance. In order to obtain the best results, using the resonance method, the capacity should be adjusted to the inductance of the oscillating circuit, until a maximum output of energy takes place. Low coupling is essential to the success of the method.

As a matter of fact, we do not even have to know the magnitude of the inductances and capacities that produce resonance, for the cell whose capacity is to be measured is connected in parallel with the standard precision condenser used to adjust the circuit to resonance. If the second circuit is brought to resonance, using the precision condenser with the dielectric cell disconnected, a certain capacity is indicated by it. Then, if the dielectric cell is connected into the circuit, the capacity contributed by the standard precision condenser will have to be reduced by the amount of the capacity introduced into the circuit by the dielectric cell to return the circuit to resonance.

A suitable dielectric cell may be described briefly as follows: It consists of a set of fixed plates and a set of rotor plates of heavily silver-plated brass properly spaced and semicircular in shape. The end pieces are of heavy molded bakelite or of pyrex glass. The shaft is of steel and has cone bearings accurately machined and positively locked in position to assure perfect alignment and reproducibility of rotor position. A brass pointer is fastened directly to the shaft and rotates with it above a circular brass scale. The divisions of the scale are such that the pointer may be reset to any position, well within the accuracy of the standard precision variable condenser, which is used to determine the capacity differences between the several rotor positions of the dielectric cell. The condenser proper is attached to a bakelite or glass cover which fits over the glass containing vessel. It is preferable to use oil, rather than water, in the thermostat bath. The position of the dielectric cell in the thermostat should be always the same.

In order to use the equation $\epsilon = C_x/C_a$ for accurate determination, elaborate calibrations for lead-wire and stray-capacity effects are

necessary. For the work of the laboratory, it is convenient to use a dielectric cell which is arranged so that capacity measurements can be made with a variable condenser, rather than with one having fixed plates. Measurements can then be made of capacity differences between two fixed positions of the rotor plates (a and b), first when the plates of the condenser are in air, and then when they are immersed in the liquid or solution.

The dielectric constant of the liquid is obtained by dividing the difference in capacity between the positions a and b when the plates are immersed in the liquid by the difference in capacity with air between these positions, or

$$\epsilon = \frac{C_{b(\text{liquid})} - C_a}{C_{b(\text{air})} - C_{a(\text{air})}}$$

In the actual measurement the exact amount of capacity introduced by moving the rotor from a to b must be removed from the precision
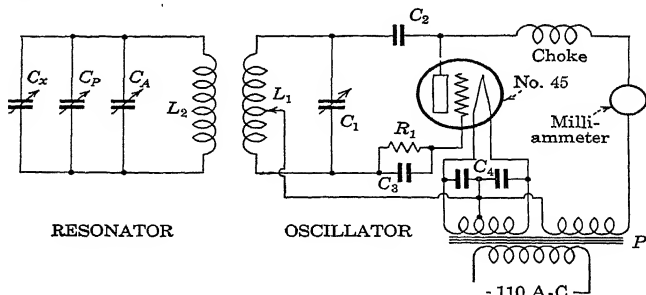
FIG. 52.—Resonance circuit for measuring dielectric constant.

condenser in order that the circuit may be in resonance with the generator both before and after changing the position of the rotor in the dielectric cell; thus the capacity differences necessary for the dielectric-constant calculations are made available. The resonance circuit for measuring dielectric constants is shown in Fig. 52.

The essential parts of the generator circuit are the inductance L_1 and capacity C_1. The inductance consists of approximately 30 turns of either No. 12 copper wire or small copper tubing wound on a tube of 3 in. diameter. The tap indicated (Fig. 52) is taken off about 10 turns from the plate end. The generator operates entirely from the 110-volt a-c line, an ordinary power transformer supplying both the filament current and plate voltage for the No. 45 vacuum tube. The plate circuit must be provided with a choke coil for operation in

this way. The condensers C_4, although not absolutely necessary, serve to stabilize the frequency and are therefore advisable. In the grid circuit, a capacity C_3 and bias R_1 are used. The milliammeter in the plate circuit of the vacuum tube serves to indicate the resonance condition.

The resonating circuit may be coupled to the generator either by capacity or, as we indicate here, by inductance. The three condensers in this circuit are connected in parallel; thus, their individual capacities add to give the total capacity. The condenser C_p is a precision instrument of 1,000 to 1,500 $\mu\mu f$ capacity. An auxiliary condenser C_A is included, in order to permit readings of the capacity difference, between positions a and b of the dielectric cell C_x, to be made on different parts of the scale of the precision condenser. For all accurate work, it is absolutely necessary to calibrate the precision-condenser readings in terms of capacity. For this laboratory experiment, it will be sufficient to assume differences in scale readings to be proportional to capacity differences, provided that these observations are not made near the low or the high ends of the scale. Positions of resonance are indicated by the sharp dip of the milliammeter reading in the oscillator circuit.

The experimental data necessary for the electric-moment calculations are the dielectric constants and densities of benzene and of dilute solutions of chlorobenzene, nitrobenzene, or other polar molecule in benzene at 25°C. Concentrations suggested for the work are 3, 4, 5, 7, and 10 mole per cent of solute. The density determinations may be made pycnometrically or with a Westphal balance (pages 321 and 322).

Calculations.—The electric moment of a solute molecule surrounded by the inert molecules of a nonpolar solvent may be calculated in the following manner: The molar polarizations of the solute molecule P_2, for the several concentrations, are obtained from the equation

$$P_2 = \frac{}{f_2}$$

already presented in the theoretical section. The molar polarization of the solute molecule in infinitely dilute solution in the nonpolar solvent is obtained by extrapolation to zero concentration of the curve obtained when these P_2 values are plotted as a function of the corresponding mole fractions of the solute. This limiting value P_2^0, characteristic of single solute molecules, contains two terms: a polarization due to its orientation in the electrical field, and a polarization due to its deformation. The latter can be approximated from refractive index and density data, or from tables of atomic refractions.

Then

$$P_2 = P_{2(\text{deformation})} + P_{2(\text{orientation})} = \frac{n_D{}^2 - 1}{n_D{}^2 + 2} \cdot \frac{M}{d} + P_{2(\text{orientation})}$$

or

In this equation, n_D is the refractive index of the solute molecule for the D line. For use in the equation, refractive index and density data for a single temperature are required.

The value of $P_{2(\text{orientation})}$ having been determined, the calculation of the electric moment of the molecule follows directly, for

$$P_{2(\text{orientation})} = \frac{4\pi N \mu^2}{3kT}$$

or

$$\mu = 0.0127 \times 10^{-18} \sqrt{P_{2(\text{orientation})} \times T}$$

Practical Applications.—Electric-moment data have contributed much to the solution of chemical and physical problems. Since the electric moment is a measure of the electrical symmetry or lack of symmetry in a molecule, it is not strange that these data have been of much value in connection with problems of molecular structure. They have also contributed to improve our understanding of association and compound formation in solution, of directive influences in reactions of organic chemistry, and of energy losses in commercial dielectric materials.

Suggestions for Further Work.—The electric moments of a series of ortho-, meta-, and para-like disubstituted derivatives of benzene may be determined to show the effect on polarity of a change of position of groups within a molecule.

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63. Dielectric Constant and Dipole Moment. Capacity Determinations by Heterodyne-beat Method

The heterodyne-beat method of determining the dielectric constant of a solution is most commonly used by chemists for dipole moment studies. It is illustrated in this experiment.

Theory.—In order to obtain the electric moment of a molecule by using the solution method, dielectric-constant and density determinations are required. The pertinent theory has been outlined in Exp. 62. For accurate measurements of the dielectric constants of liquids and solutions having extremely low conductance, the heterodyne-beat method is probably the best available at the present time. The principle upon which it is based may be described as follows: The frequency at which an electron-tube oscillator operates is a function of the inductance, capacity, and resistance of the circuit. If two oscillators that operate at frequencies nearly alike are loosely coupled, each circuit will induce currents of its own frequency in the other. The currents in each circuit will heterodyne, or combine with each other to produce beats of a frequency equal to the frequency difference between them. This beat frequency can be controlled by adjustment of the capacity in one of the circuits and be brought into the audible range. If one circuit is maintained at fixed frequency and the other one operates at a slightly higher frequency, an increase in the capacity in the latter causes a decreased frequency and therefore a decreased beat frequency. Further increase in this capacity eventually lowers the frequency of the measuring circuit below that of the standard oscillator. By careful adjustment of the capacity, the frequency of this circuit approaches and becomes equal to that of the standard generator, and no beats can be detected. The precision condenser of the measuring circuit may, therefore, be sharply adjusted to the point that brings silence in the detector while the rotor plate of the dielectric cell is maintained at some definite position a. If the rotor of the dielectric cell is now moved to position b, thereby increasing its capacity, an amount of capacity exactly equal to the difference in capacity between positions a and b will have to be subtracted by means of the precision condenser to bring the frequency of the measuring circuit back to that of the standard generator, for the condensers are connected in parallel. Thus, the dielectric constant of a liquid or solution may now be obtained by using the equation and method outlined in Exp. 62, because there can be determined capacity differences between the rotor positions a and b of the dielectric cell with the plates in air or immersed in pure liquid or solution. The

equation is

$$\epsilon = \frac{C_{b(\text{liquid})} - C_{a(\text{liquid})}}{C_{b(\text{air})} - C_{a(\text{air})}}$$

Apparatus.—The various elements of two alternative assemblies for dielectric-constant determinations using the heterodyne-beat method are connected as
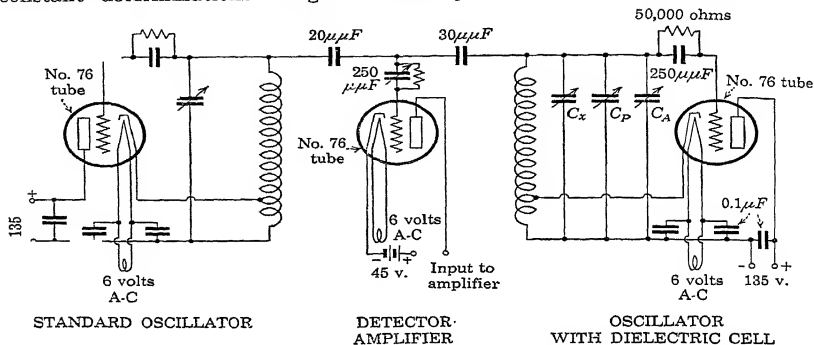
FIG. 53.—Heterodyne heat circuit for measuring dielectric constant.
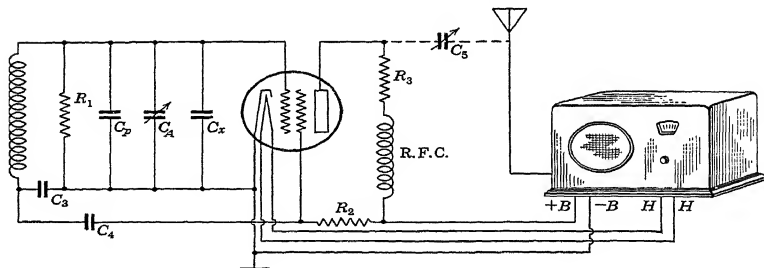
FIG. 54.—Heterodyne heat circuit for measuring dielectric constant by using a commercial radio set.

shown in Figs. 53 and 54. The second of these assemblies is especially simple since it makes use of an ordinary and inexpensive radio receiver for the detector-amplifier portion of the circuit, and the carrier wave from a near-by broadcasting station as a source of oscillations of constant frequency.

In addition, there are required pycnometer, nonpolar solvent media, and various polar substances. The latter may be liquids of the type nitrobenzene and chlorobenzene, or they may be solids such as the monosubstituted halogen derivatives of naphthalene.

Procedure.—In making the capacity measurements, the condensers C_p, C_x, and C_A, connected in parallel, are manipulated in the manner described in the previous experiment, except that now the

capacity of the circuit containing these condensers is varied until the beat note observed in the telephone receiver (or loudspeaker) has been reduced to zero frequency rather than to the point of resonance. In either case, the natural frequencies of the two circuits have been adjusted to equivalence.

The dielectric constants of the dilute benzene or hexane solutions of the substance whose electric moment is desired are determined, using the method and apparatus described above.

Calculations.—After density data are made available, the molar polarizations for the solute P_2 are calculated and plotted as a function of concentration. This curve is extrapolated to zero concentration, where any mutual interaction of the dipoles vanishes. The molecular refractivity for the solute molecule is determined either from refractive index and density data, using the Lorenz-Lorentz formula (page 46), or by adding the atomic refractions, obtained in standard tables, to give directly the molecular refractivity. On the assumption that the polarization due to orientation may be obtained by subtracting the optical or deformation part from the total polarization, the electric moment of the solute molecule may now be calculated. Reference to the text of Exp. 62 will help to clarify the details of this calculation.

Practical Applications.—The introduction of the heterodyne-beat method for the determination of the dielectric constant has made possible for the first time really accurate determinations of the electric moments of gaseous molecules. With the increased accuracy obtainable in the case of liquids, it is possible to study the effect of change of a nonpolar solvent on the magnitude of the electric moment for a given solute molecule. A slight, but definite, dependence upon dielectric constant of the solvent medium has been established.

Suggestions for Further Work.—In order to demonstrate the applicability of the solution method for the determination of the electric moment of a substance ordinarily considered as gaseous, and at the same time to compare the result with that recorded in the literature and obtained by using the more proper method depending upon the temperature coefficient of the dielectric constant of the vapor, measurements may be made upon solutions of dry hydrogen chloride in dry benzene. The concentrations of gas in the solutions can be estimated by titration.

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CHAPTER XIV

ISOTOPES AND EXCHANGE REACTIONS

64. Exchange Reactions with Radioactive Lead

Radioactive isotopes of lead are prepared and used in tracer experiments, including the determination of the solubility of lead chromate.

Theory.—By labeling certain molecules in a group of molecules and following them through various chemical and physical changes many important facts can be discovered. The use of isotopes as indicators or tracers for the heavy elements radium and thorium and their disintegration products was first developed about 30 years ago. This technique has been steadily increasing in importance as new applications have been developed. Since the discovery of deuterium and the production of artificial radioactivity in 1932, the use of isotopic tracers has increased greatly, particularly in the field of biology. The development of a very sensitive device for detecting traces of radioactivity, the Geiger-Mueller counter, has done much to accelerate the development of this work.

In this experiment the naturally occurring radioactive heavy elements are studied, and in a later experiment an artificially radioactive element is used.

Radium D with a half-life of 22 years or thorium B with a half-life of 15 hr. are isotopes of lead giving off beta rays that are especially suitable for measurement. Their chemical properties and reactions are practically the same as those of ordinary lead.

Apparatus.—Geiger-Mueller chamber and counter or electroscope with ionization chamber; radioactive lead or radiothorium and source of 200 or more volts, or old hospital capillaries from radium treatment; lead nitrate, potassium chromate.

Procedure.—If radiothorium is available, a small sample is placed in a test tube and the emanation (thoron) diffuses up into the tube where its decomposition products thorium A and B are collected on a platinum wire which is inserted through the stopper. The wire is charged negatively at 200 to 500 volts with B batteries, rectifier and transformer, or a dynamo.

The positive terminal is attached to metal foil which lines the tube, and practically no current is drawn. Several hours may be necessary to collect a sufficient quantity of thorium B. Of course it is too small to see or weigh, but it can be followed by its radioactivity. After the wire has collected this small deposit, it is placed in about 25 ml of $0.001M$ lead nitrate solution for about half an hour. The deposit dissolves and mixes with the ordinary lead, giving a solution of lead that exhibits considerable radioactivity.

Radioactive lead which is commercially available is satisfactory for this experiment if a Geiger-Mueller counter is available. A small piece of 0.1 g is dissolved in concentrated nitric acid, evaporated, and dissolved in water.

Another alternative source of radioactive material is the capillary radon tubes discarded by hospitals that give radium treatments. Six or more tubes are washed in carbon tetrachloride to remove wax and then ground in a mortar. The pulverized glass containing the film of decomposition products from radon is heated in a small crucible under a hood to drive off mercury and wax but not enough to cause sintering. The material is then placed in a paraffin container and dissolved in hydrofluoric acid. After complete solution, it is diluted with an equal volume of water and a strip of silver foil is placed in the solution for a few hours or overnight. The invisible film of radioactive lead deposited on the silver is then removed by dipping briefly into dilute nitric acid and mixed with about 25 ml of $0.001M$ lead nitrate solution. The silver is precipitated with a drop of dilute hydrochloric acid and filtered.

A definite quantity, 5 ml, of the solution, containing the lead nitrate and the radioactive lead, is carefully evaporated to dryness on a one-inch watch glass. The dish fits snugly into the chamber of an electroscope or a Geiger-Mueller counter (page 388), so that the position of the active deposit in the bottom will always be the same. The rate of fall of the electroscope leaf in divisions per minute or the number of counts registered per minute on the electric amplifying circuit and relay of a Geiger-Mueller chamber is recorded. If the radioactivity is too small, it is necessary to use more radioactive material or a more sensitive detector. A correction is necessary for stray radioactivity, cosmic rays, and electrical leakage. The activity in the absence of the radioactive lead is subtracted from the radioactivity in its presence. A second determination is made as a check.

An exactly equivalent amount of potassium chromate is mixed with 5 ml of the isotopic lead nitrate solution and allowed to stand in a thermostat until the precipitate of lead chromate has settled. Then

5 ml of the clear solution is drawn off and evaporated to dryness in a shallow dish as before.   A small filter paper is tied over the pipette, if necessary, to keep out particles of the precipitate.   The radioactivity of the slight residue is obtained as before in terms of the number of scale divisions per minute passed by the electroscope leaf, or the number of counts recorded with the Geiger-Mueller chamber.

The determinations of radioactivity should be made nearly at the same time, because the material may lose its radioactivity.

Although qualitative in nature and unconnected with the preceding experiment, one other experiment is performed because it constitutes such an excellent proof of the electrolytic-dissociation theory.   A small crystal of lead chloride is added to the solution of the preceding experiment, containing the radioactive lead.   The solution is heated to dissolve the crystal, and then the lead chloride is crystallized from solution by cooling.   The lead chloride is carefully rinsed and tested for radioactivity.   Although inactive originally, it becomes radioactive in this treatment by exchanging some atoms of ordinary lead for atoms of radioactive lead.   This interchange of atoms is possible if lead nitrate and chloride dissociate in solution into lead ions, which then exchange partners with the anions.

In a nondissociating solvent, which does not conduct the electric current, this exchange is impossible.   For example, lead tetraphenyl crystallized from a solution of radioactive lead in pyridine exhibits no radioactivity.

Calculations.—The radioactivity r of the residue, in terms of the number of counts s on the relay of the Geiger-Mueller counter, or the number of corrected scale divisions s per minute, is proportional to the number of atoms of radioactive lead, and hence is proportional to the total number of lead atoms.   The concentration c_o of lead in the original solution is known, and from the following proportion it is easy to calculate the concentration of lead in the mother liquor c_M or, in other words, the solubility of the lead chromate.

$$\frac{s_M}{s_o} = \frac{r_M}{r_o} = \frac{c_M}{c_o}$$

The subscript M refers to the mother liquor after precipitating out the lead chromate, and the subscript o refers to the original solution.

The radioactivity readings are corrected for background activity by subtracting from them the readings obtained when the sample is removed from the counting chamber.

Practical Applications.—Radioactive indicators are used in many different ways, which are summarized by Paneth[1] and by Hahn.[2]   The drainage of pipettes

and burettes, the adsorption of salts by precipitates, the permeability of cloths to gases, the existence of rare hydrides (*e.g.*, hydrides of tin and lead), and the absolute surface of powders are among the problems that have been successfully studied with radioactive indicators.

Suggestions for Further Work.—The absolute surface of 1 g of lead sulfate powder may be determined.[3] A saturated solution of radioactive lead sulfate is used. It is shaken for 2 hr. or more with freshly precipitated lead sulfate, which has not been allowed to dry out. If the precipitate is allowed to dry out, the cracks between the crystals will be closed up. The crystals are allowed to settle, and the radioactivity of the solution is determined before and after treating with the lead sulfate crystals, evaporating samples to dryness as previously described. The decrease in activity is due to the replacement of lead sulfate at the surface of the crystals by lead sulfate in solution. The solubility of the lead sulfate is determined experimentally, or taken from tables, and the weight of lead sulfate on the surface is calculated from the following proportion:

$$\frac{\text{Weight of lead sulfate on surface}}{\text{Weight of lead sulfate in solution}} = \frac{\text{activity of crystals}}{\text{activity of solution}}$$

The activity of the crystals is obtained by subtracting the activity of the final solution from the activity of the original solution.

The weight of lead sulfate on the surface is divided by the atomic weight of lead and multiplied by 6.02×10^{23} to give the total number of atoms of lead on the surface of this particular sample. The area may be expressed in square centimeters by multiplying the number of atoms by the cross section of the lead sulfate molecules obtained from crystallographic data. Full details and a sample calculation are given by Koehler and Mathews.[3]

The amount of lead nitrate occluded in precipitates of different kinds is easily determined by the method of radio indicators. The exchange of ions on precipitates has been studied by Kolthoff.[4,5]

The isotope of thorium UrX_1 giving off beta rays with a half-life of 24.5 days may be prepared by shaking uranyl nitrate with its water of crystallization with ether. Of the two liquid layers that form, the ether layer on top contains most of the uranium and the water layer contains most of the uranium X_1. The water layer is drawn off in a separatory funnel for experimental tests, whereas the uranyl nitrate is recovered by evaporating and recrystallizing from a little water. Solubilities and exchange reactions with thorium compounds and diffusion rates may be studied.

Radio indicators can be used to determine end points in titrations, sucking up the solution after each addition of reagent through a fritted glass filter into a Geiger-Mueller chamber and returning it again.[7]

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65. Exchange Reactions with Radioactive Bromine

This experiment involves the nuclear reaction of a common element, bromine, and the application of this radioactive isotope to chemical problems. The use of a high-voltage generator, a cyclotron, or a supply of radium is necessary.

Theory.—One of the most interesting of the recent developments in physical chemistry has been the use of isotopes of the common elements as tracers. With these marked atoms, which have practically the same chemical properties as the unmarked ones, it is possible to follow a given group of atoms through various chemical and physical changes. Already a large number of physicochemical theories have been tested by this means.

Isotopes can be followed and their concentrations determined by virtue of their different mass or by their radioactivity. Naturally occurring radioactive isotopes have been used as tracers for many years,[1,2] but radioactive isotopes of the common elements have been available only since 1934. They can be produced by neutrons from the action of alpha rays from radium on beryllium, or from ions of hydrogen or deuterium accelerated at very high voltages by cyclotrons or by electrostatic generators operating in the neighborhood of a million volts.

Parallel with the development of a means for producing radioactive elements has been the development of extremely sensitive apparatus for measuring the radioactivity of isotopes even when the quantities of material are too small to weigh or determine in any other way.

Bromine with its many interesting reactions, characteristic of the halogens, is a suitable element for tracer experiments because one of its radioactive isotopes has a conveniently long life (40 hr.) and because by virtue of a chemical change it can be easily separated from the unchanged bromine compound and concentrated.

Ordinary bromine has isotopes of atomic weight 79 and 81, present in about equal proportions. The most convenient radioindicator of bromine is made with neutrons according to the reaction

$$_{35}\text{Br}^{81} + {}_0n^1 \rightarrow {}_{35}\text{Br}^{82} + \gamma$$
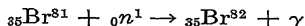
This new isotope of bromine is unstable, and it decomposes with a half-life of 39.9 hr. into krypton giving off beta rays e^- and gamma rays γ according to the reaction

$$_{35}\text{Br}^{82} \rightarrow {}_{36}\text{Kr}^{82} + e^- + \gamma \qquad t_{\nu} = 39.9 \text{ hr.}$$
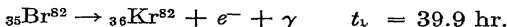
There is a complication for when the bromine isotope $_{35}Br^{79}$ captures a neutron two additional radioactive isotopes are formed.

$$- {}_0n^1 \begin{cases} \nearrow \gamma + {}_{35}Br^{80} \text{ (4.4 hr. half-life)} \rightarrow \gamma \text{ or conversion electron.} \\ \searrow \gamma + {}_{35}Br^{80} \text{ (18 min. half-life)} \rightarrow {}_{36}Kr^{80} + e^- + \gamma \end{cases}$$
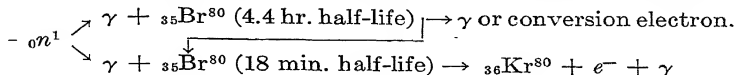
All three of these radioactive isotopes are present in bromine that has been subjected to neutron bombardment, but by waiting 12 to 24 hr. the 4.4-hr. and the 18-min. bromine become weak, whereas the 39.9-hr. bromine loses less than half of its radioactivity. Any first-order reaction will be 99 per cent completed in 6 to 7 half-lives. Tracer experiments are complicated by the fact that one of these isotopes is active and is not characteristic of an inert bromine atom. The difficulty is removed by waiting 24 hr. after the neutron bombardment. This phenomenon is not common because in only a few elements is it possible for one radioactive isotope to change over into another isotope of the same element. This chemically active isotope of bromine offers interesting possibilities for special experiments.[3]

Fast neutrons are ineffective in nuclear reaction of bromine, and they must be slowed down by passage through material containing hydrogen either in the form of a screen or in the form of a hydrogen-containing molecule which comprises the target itself. Hydrogen is particularly effective because it has the same atomic weight as the neutrons.

In some cases, isotopic atoms will exchange with atoms of the same element in other compounds, and sometimes they will not. In general, exchange will take place if both atoms ionize or dissociate and can be shuffled around in the reaction vessel. Again, if a chemical compound or complex or an adsorption compound is formed there may be a chance for exchange of atoms.

Apparatus.—Source of neutrons (0.2 g radium mixed with beryllium, or cyclotron, or high-voltage generator); Geiger-Mueller ionization tube and amplifying circuit; impulse counter; electric clock or stop watch; 2 liter supply ethylene dibromide; 2-liter bottle; 2-liter separatory funnel; one 100-ml separatory funnel; $0.05N$ NaBr; $0.05N$ Br_2; $0.05N$ $NaBrO_3$; $0.5N$ $AgNO_3$; sodium sulfite; 2-cm Gooch crucible; filter paper to fit Gooch crucible; dilute collodion.

Procedure.—This experiment can be carried out only when a source of neutrons is available. A small metal capsule containing 0.2 g of radium mixed with beryllium is a convenient source. It is merely suspended for a day in the center of a 2-liter bottle filled with ethylene dibromide. Ethyl bromide may be used but it is less effective. An exposure of 48 hr. or more is recommended. Half the

maximum activity will be obtained in 39.9 hr. and three-fourths in 79.8 hr.

Cyclotrons or other high-voltage apparatus for disintegrating atoms are available in the physics laboratories of several universities. Radioactive bromine may be obtained by setting a bottle of ethylene dibromide in the path of the neutrons for a short time, the length of the exposure depending on the intensity of the neutron source. Sufficient activity may often be produced even by setting the bottle near a neutron source which is operating in connection with some other experiment.

After exposure the liter of ethylene dibromide is extracted with a portion of about 100 ml of water containing 0.05 mole per liter of sodium or potassium bromide as a carrier. The radioactive material is much too small in quantity to be seen, and it is necessary to add a sufficient quantity of material to carry out the laboratory operations. When a bromine nucleus is disintegrated by capture of a neutron, sufficient energy is released by the recoil from the gamma ray to decompose the molecule that contains it and liberate the bromine. The bromine is liberated as an atom or in a form that combines in such a way as to give bromide ions in aqueous solution. The aqueous solution of radioactive bromide is then diluted to 250 ml, and 10- to 50-ml samples are used for the several experiments,* depending on the intensity of radioactivity and the sensitivity of the counter.

The samples are treated in various ways and then tested for radioactivity by treating with silver nitrate and placing the solid silver bromide in the chamber of the Geiger-Mueller counter. Slightly more than 5 ml of $0.5N$ $AgNO_3$ is added to the 50-ml sample, and the solution is heated to boiling to coagulate the precipitate. It is filtered with suction onto a small filter paper in a Gooch crucible about 2 cm in diameter, washed, and rinsed. A small Hirsch suction funnel is convenient but not necessary. The filter paper is removed and spread flat on a piece of blotting paper, and the precipitate is spread out uniformly with a glass rod, care being taken to retain all the precipitate on the filter paper. A thin layer of very dilute collodion is made to flow over the precipitate to prevent scattering and loss when the precipitate dries out. The paper with the precipitate is then transferred to the chamber below the Geiger-Mueller counter (page 389), and the number of counts recorded over a suitable period (10 min.) is noted.

More accurate results are obtained by centrifuging out the silver bromide. The precipitate is transferred to a one-inch watch glass and dried.

* The organic material may be removed by fusing the sodium bromide in air.

The Geiger-Mueller ionization tube is connected with an electron tube circuit and an impulse counter which turns a numbered wheel by means of an electric magnet each time that a beta ray passes through the chamber. The gamma rays are so penetrating that they have but slight ionizing effect on the low-pressure gas in the tube. An electric clock in the circuit of the impulse counter offers a convenient way of obtaining accurately the average number of counts per minute. It is necessary to make a correction for the cosmic rays or other ionizing agents in the laboratory by measuring the "background" number of counts per minute just after or just before inserting the radioactive material in the counter chamber.

Counts are determined on the precipitated silver bromide from a sample of the solution shortly after removal of the ethylene bromide from the neutron bombardment. If the radioactivity of this sample is determined at intervals of 10 min. for an hour and then at intervals of half an hour for a few hours, a composite decay curve can be plotted for the mixture of the 18-min., the 4.4-hr., and the 39.9-hr. bromine.

The rest of the experiments should be carried out after the solution of radioactive bromide has stood for at least 12 hr. or more to allow for the decay of the 4.4-hr. bromine which is chemically active.

To another sample is added an equal volume of a $0.05N$ bromine solution made acid with sulfuric acid ($0.05N$), and tightly stoppered in order to ascertain whether or not there is an exchange between bromine molecules and bromide ion in aqueous solution.[4] The solutions of bromine are kept tightly stoppered to prevent evaporation of the bromine. After mixing and standing for 10 min. the bromine is extracted in a separatory funnel with two or three portions of about 10 ml of carbon tetrachloride until no color is left in the aqueous solution. The aqueous solution is precipitated with silver nitrate. The carbon tetrachloride solutions are then extracted with dilute sodium sulfite solution until all the bromine has been removed and converted into bromide ions. The aqueous solution is then acidified slightly with nitric acid and precipitated with silver nitrate. Counts are determined in quick succession with the silver bromide from the aqueous solution, the carbon tetrachloride extract, the control, and the empty Geiger-Mueller chamber.

To determine whether or not bromide ion will exchange with bromate ion, 50 ml of the radioactive bromide solution is mixed with 50 ml of a slightly alkaline solution of $0.05N$ sodium bromate and precipitated with silver nitrate. The silver bromate is soluble in these concentrations, and may be recovered by evaporating the filtrate to dryness and collecting the residue by mopping up with a moist filter

paper. The counts are determined with the precipitated silver bromide, the bromate, the control, and the empty chamber.

If time permits, the exchange is measured when bromine together with carbon tetrabromide are illuminated. Bromine atoms are produced by the illumination. It is necessary in this experiment to bubble out the dissolved oxygen with nitrogen or hydrogen.

Calculations.—The readings on the impulse counter connected through an electron-tube amplifying circuit to the Geiger-Mueller apparatus are calculated in terms of counts per minute, and the value obtained with the empty chamber is always subtracted from the value obtained with a radioactive sample. This difference is proportional to the radioactivity. Since equal portions of the bromide solution (50 ml of $0.05N$ solution) were always taken, the relative counts per minute give a direct measure of the exchanges. If the portions or the compositions are unequal, equilibrium calculations must be applied.

The experiments show whether or not exchange of atoms occurs between bromide ion and bromine, and between bromide ion and bromate ion. If exchange does occur, equations for the chemical or ionization reactions are to be suggested.

The decay curve is determined after a 24-hr. delay and activity due to this 39.9-hr. bromine during the first few hours is calculated. The activity of the 18-min. and the 4.4-hr. bromine is determined by subtracting the activity of the 39.9-hr. bromine from the total observed activity.

Suggestions for Further Work.—Several interesting exchange reactions may be tested such, for example, as the following:

Bromide ion and tribromoacetate ion in water solution.

Bromide ion in sodium bromide, and silver bromide in a mixture of the fused salts.

The aging of a surface of silver bromide precipitate in contact with bromide ions may be investigated.

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66. Exchange Reactions with Isotopic Hydrogen

The use of a heavy isotope in tracer experiments is illustrated.

Theory.—Hydrogen of atomic weight 2, named deuterium, occurs in ordinary hydrogen to the extent of about 1 part in 5,000. The existence of this heavier isotope of hydrogen was discovered by Urey. Although the chemical reactions of isotopes are nearly identical, there are very minor differences which show up most prominently in the elements of low atomic weight, and especially in hydrogen. When water is electrolyzed, the hydrogen comes off at the cathode more easily than deuterium, and by fractional electrolysis on a large scale it is possible to prepare pure deuterium oxide D_2O. Other methods, such as fractional distillation on a large scale, may be used also to produce an enrichment of the heavier water.

The theoretical limits in the concentration of isotopes can be illustrated with the following calculations on deuterium.

In a mixture of water containing equal parts of the light isotope H and the heavy isotope D, it is found that H is liberated by electrolysis about five times as fast as D. In more general terms

$$= 0.2$$

If N_H, N_D, and V designate, respectively, the atomic fractions of the two isotopes and the volume of water after electrolysis, and N_H^0, N_D^0, and V^0 refer to the same quantities before electrolysis, it can be shown that

$$\left(\frac{V}{V^0}\right)^{1.0-0.2} = \frac{N_D^0}{N_D}$$

Until the water has been electrolyzed to such an extent that N_D amounts to a few per cent, the ratio N_H/N_H^0 is practically unity and the formula connecting the decreased volume produced by electrolysis with the concentration of the heavy hydrogen reduces to

$$\log \frac{N_D^0}{N_D} = 0.8 \log \frac{V}{V^0}$$

A. Concentrated Deuterium Oxide*

Apparatus.—Heavy water containing over 99 per cent deuterium oxide; 10-ml weighing bottle; balance; desiccator; wide-mouthed beaker fitted with two-hole rubber stopper; drying tube of calcium chloride; two gas washing bottles.

* Two procedures are suggested. The first is simpler but more expensive.

Procedure.—Approximately 0.9 g of urea (about $\frac{1}{60}$ mole) is weighed accurately in a weighed 10-ml weighing bottle and heated to constant weight. After heating for 5 to 10 min. in an oven at 105° with cover removed, the sample is cooled in a desiccator, stoppered, and weighed. The process is repeated until two successive weighings agree within 0.2 or 0.3 mg. When the weight has become constant, about 2 g of deuterium oxide is introduced into the weighing bottle with the urea, and the bottle is stoppered and weighed accurately.
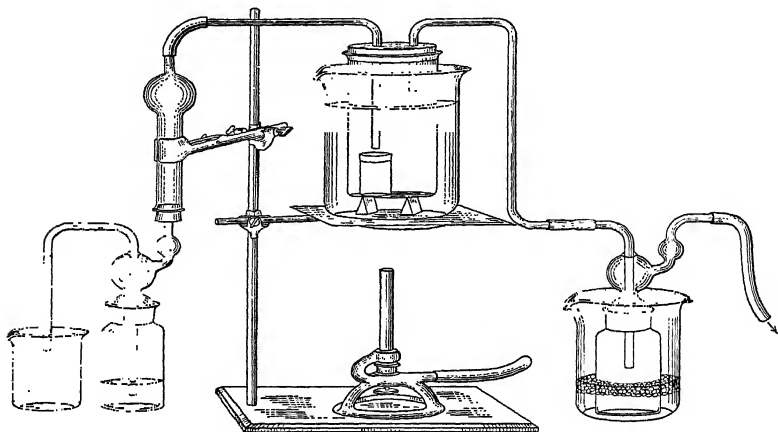
Fig. 55.—Apparatus for studying exchange reactions with heavy hydrogen by direct weighing.

The weighing bottle containing the urea and deuterium oxide is then shaken gently until the urea has dissolved. It is then unstoppered and lowered into a lipless beaker or cut-off bottle provided with a two-hole rubber stopper. (A glass-stoppered gas washing bottle is satisfactory if the mouth is sufficiently wide.) The container with the weighing bottle and urea is then set into a hot-water bath as shown in Fig. 55 in order to evaporate the deuterium oxide uncontaminated by the moisture of ordinary water from the air. A water aspirator draws air through a sulfuric acid bottle, which serves both as a dryer and a bubble counter for estimating the rate of gas flow, and then through a tube of ascarite or soda lime which removes water and also carbon dioxide, which might aid in the hydrolysis of urea. The small washing bottle surrounded by ice and salt serves to recover much of the diluted deuterium oxide.

When the water has been evaporated, the weighing bottle with the urea residue is heated at 105° to constant weight as before. The bottle is kept stoppered during weighing and storage.

The increase in weight of the urea after dissolving in the heavy water and evaporating is due to the substitution of hydrogen by deuterium.

Calculations.—It is desired to determine how many of the four hydrogen atoms in the urea molecule can be replaced by deuterium. This number can be interpreted in terms of molecular structure. If the urea were in equilibrium with pure deuterium oxide, all the replaceable hydrogens would be replaced by deuterium. However, the pure deuterium oxide becomes diluted with ordinary water by the exchange with hydrogen from the urea. Since the urea and heavy water are in equilibrium, the mole fraction of replaceable hydrogens which are replaced by deuterium will be equal to the mole fraction of the deuterium oxide in the water which is in final equilibrium with the urea. Dividing the apparent number of hydrogen atoms replaced by the mole fraction then gives the maximum number of hydrogen atoms A that can be replaced, *i.e.*, the number that would be replaced if the urea were in equilibrium with pure deuterium oxide.

Then

$$A = (u_2 - u_1) \frac{60/u_1}{n_{D_2O}/(n_{D_2O} + n_{H_2O})}$$

where A is the number of hydrogen atoms replaced by deuterium per molecule of urea, u_1 is the weight of original urea, and u_2 is the weight of urea after dissolving in heavy water and evaporating.

The mole fraction $\dfrac{n_{D_2O}}{n_{D_2O} + n_{H_2O}}$ is calculated from the original weight w of the deuterium oxide (assumed to be pure) and the molecular weights 18 and 20 of water and deuterium oxide.

Thus

$$n_{H_2O} = \frac{u_2 - u_1}{2}$$

$$n_{D_2O} = \frac{w}{20} - \frac{u_2 - u_1}{2}$$

B. Dilute Deuterium Oxide

Apparatus.—Heavy water containing about 5 per cent deuterium oxide; pure ethylene glycol; pycnometer (10 ml); 50-ml distilling flask; condenser; 1° thermometer; still head.

Procedure.—The density of the heavy water is determined to better than 1 part in 10,000 by means of a 10-ml pycnometer of the Ostwald Sprengel type shown in Fig. 27.   Additional directions for the use of the pycnometer are given on page 322.   If a pycnometer is not available, one can be made from a 10-ml pipette by bending the tubes as shown in Fig. 27, on page 96, and drawing them down to capillary size (0.5 mm) at the end and at the point where the mark is to be made. A more accurate type is shown on page 323.

The volume of the pycnometer is obtained by weighing the pycnometer filled with redistilled water after setting to the mark while immersed in a thermostat at 25°.   The density of water at 25° is 0.997044.   Check determinations of the weight should agree closely.

Ethylene glycol is purified from water by distillation, and about 0.2 g of it and about 15 g of the heavy water containing 5 per cent or more D_2O are weighed out into a small weighing bottle, weighing to the closest mg.   The deuterium of the water exchanges immediately with part of the hydrogen in the ethylene glycol.   The water is distilled off with an efficient fractionating column and collected.   To ensure that no ethylene glycol is carried over, the distillation is stopped before any rapid rise in temperature occurs.

The condensed water is redistilled after adding a trace each of sodium hydroxide and potassium permanganate, and its density is determined as before in the pycnometer.

If heavy water is allowed to stand for more than a few minutes, it must be stoppered to prevent exchange with ordinary water in the moisture of the air.

Calculations.—The specific gravity of D_2O at 25° is 1.1079 times as great as the specific gravity of ordinary water.   The specific gravity of a mixture of H_2O and D_2O increases at a rate directly proportional to the mole fraction X of the deuterium oxide in the mixture.   Then the mole fraction can be calculated from the difference between the specific gravity of the mixture S and that of ordinary water S_{H_2O}.[3,4] Thus

$$S - S_{H_2O} = 0.1079X$$

When a hydrogen-containing substance is placed in heavy water, there may be an exchange of its hydrogen atoms with the deuterium atoms of the water.   If there is such an exchange, the specific gravity S of the heavy water will decrease to S', and $S - S'$ represents the extent of the exchange.   The maximum possible change $(S - S')_{max.,}$ caused by a complete exchange of all the hydrogen of the solute with the deuterium of the heavy water, depends on the number of hydrogen

atoms h in the solute molecule and on the ratio of the number of moles of solute to solvent. Thus

$$(S - S')_{\text{max.}} = 0.1079 \frac{h}{2} \frac{w_{\text{solute}}}{M_{\text{solute}}} \bigg/ \frac{w}{20\text{X} + 18(1 - \text{X})}$$

where w and w_{solute} are the original weights, respectively, of the heavy water and the solute, and M_{solute} is the molecular weight of the solute. For ethylene glycol, $C_2H_6O_2$ with a molecular weight of 62 the expression becomes

$$- S')_{\text{max.}} = \frac{0.00522 w_{C_2H_6O_2}(2\text{X} + 18)}{w}$$

The fraction γ of hydrogen atoms in the molecule that are replaceable under the conditions of the experiment can then be calculated from the decrease $(S - S')$ in the density of the water measured experimentally.

Thus

$$\gamma = \frac{S - S'}{- S')_{\text{m}}}$$

Practical Applications.—The interest in isotopic hydrogen lies chiefly in the fact that hydrogen atoms can be labeled by their greater weight and followed through various chemical reactions and physical processes. From the final distribution of the heavy and light atoms, much information can be obtained concerning the nature of the process. The applications in biology have been particularly intriguing.

Suggestions for Further Work.—Other exchange reactions may be studied such as acetone[5] with water, or carbohydrates[6] with water.

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CHAPTER XV

PHOTOCHEMISTRY

67. The Photolysis of Uranyl Oxalate

This experiment is a rather simple one which gives practice in studying the influence of several variables. The quantitative effect of time, volume, distance, and concentration of the two materials is to be determined. The experiment illustrates also the calculation of energy intensities by the use of an actinometer.

Theory.—Oxalic acid is transparent except in the shorter ultra-violet. Uranyl ions absorb light of wave length shorter than about 4,400 Å, but when they absorb light no reaction takes place, the light energy being simply degraded into heat. But when uranyl ions are mixed with oxalic acid, some loose intermediate combination takes place as shown by the fact that the absorption of light by the uranyl solution is increased by the addition of the *transparent* oxalic acid. In the mixed solution the oxalic acid is decomposed with a fairly high efficiency by the light which the uranyl ions absorb. This transfer of energy by an absorbing molecule to another molecule is sometimes called "photocatalysis." Usually the formation of some kind of a compound or loose union is necessary before energy can be transmitted from one dissolved molecule to another.

The reaction is

$$H_2C_2O_4 \qquad \cdot UO_2^{++} + H_2O + CO + CO_2$$
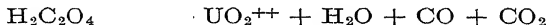
and the amount of oxalic acid decomposed is readily determined by titration with potassium permanganate before and after exposure. It is so simple to measure and so reproducible that it is widely used as an actinometer for measuring by chemical means the intensity of radiation in the ultraviolet and violet.

Apparatus.—One 100-watt capillary mercury-vapor lamp and transformer; six 1-in. pyrex test tubes; shielding box with cover; 10- and 25-ml pipette; 1 liter $0.02M$ oxalic acid; 1 liter $0.02M$ uranyl sulfate; 2 liters $0.02N$ potassium permanganate.

Procedure.—A ventilated wooden box is prepared with a cover at least 60 cm square. The inside is rendered nonreflecting by painting with lampblack in dilute shellac. Two circles are drawn with radii of

10 and 20 cm., and along each circle are bored six holes, equally spaced, for holding the 1-in. test tubes. At the center of the circles is screwed a lamp socket pointing downward. It, too, is painted dull black.

Into the socket is screwed a General Electric 100-watt H4 capillary mercury-vapor lamp (page 392), and the connection is made to the special transformer. Any quartz-mercury lamp is satisfactory for this experiment. Although the lamp is shielded by a box, special goggles must be used to protect the eyes if there is any exposure to the lamp. It is essential that the tubes hang vertically and at equal distances from the light.

The oxalic acid is weighed out accurately in preparing the solution so that it is used directly for standardizing the permanganate solution. The solutions are poured out and rinsed into Erlenmeyer flasks and acidified with dilute sulfuric acid and heated before titrating.

The six pyrex test tubes are arranged at a 10 cm distance from the capillary lamp, and each is filled with 25 ml of the oxalic acid solution and 25 ml of the uranyl sulfate solution well mixed. The lamp is turned on for half an hour, and each solution is titrated with permanganate. The titrations are compared with the titration obtained with the unexposed solution of the same concentration, and if there is a variation of more than a few per cent among the different tubes, the lamp is turned or the tubes are spaced differently so as to obtain a uniform distribution of light. It is essential that the tubes hang vertically.

The pyrex glass absorbs all the light below about 3,200 Å, but the greater portion of the light emitted by the lamp is at wave lengths longer than this. Better results are obtained with quartz test tubes.

In another experiment the six test tubes are removed one at a time after suitable time intervals: 5, 10, 20, 30, 40, 50 min.

Several successive determinations are made, usually six at a time, to determine the influence of (a) time, (b) volume, (c) concentration of oxalic acid, (d) concentration of uranyl sulfate, (e) distance. It is essential to plan the experiments carefully so that the maximum information is obtained with a minimum number of experiments, and as far as possible *only one variable is changed at a time*. Obviously, the titrations should be made while the next set of solutions is being radiated. In general, best results are obtained with a 50 ml volume of solution (made up if necessary by the addition of water) and a half-hour exposure to the light.

If the line voltage fluctuates, all six determinations will be affected equally, and even in passing from one set to another the fluctuations in intensity of the lamp will tend to average out over the half-hour periods.

Calculations.—The number of moles of acid decomposed are plotted against the time of exposure. The order of the reaction—whether first, second, or zero order—is determined. The influence of the other variables is represented graphically or mathematically in some suitable form. Explanations are then sought which will account quantitatively for the behavior of each variable.

The quantity of radiant energy absorbed in each test tube per second is calculated. The effective radiation lies between 3,200 Å the absorption limit of pyrex and 4,400 Å the absorption limit of uranyl ion, and the average is taken as 3,900 Å. The average quantum yield is 0.57 molecule of oxalic acid decomposed per quantum absorbed. The number of molecules is equal to the number of moles multiplied by 6.02×10^{23}, and the energy of each quantum is $h\nu$, or $6.62 \times 10^{-27} \times \dfrac{3 \times 10^{10}}{3.9 \times 10^{-5}}$, where h is Planck's constant, ν is the frequency of light, 3×10^{10} is the velocity of light in centimeters per second, and 3.9×10^{-5} is the wave length of centimeters.

Practical Applications.—Some of the variables in photochemical reactions are studied here.

The quartz mercury-vapor lamp is the most convenient source of ultraviolet light, and the capillary arcs are intense and inexpensive.

Ultraviolet light is used in the treatment of skin disease and rickets and for other purposes. The irradiation of foods with ultraviolet light assures an adequate supply of vitamin D. In chemical kinetics the mechanism of certain reactions may be studied by exciting the molecules photochemically instead of by simple thermal agitation.

The quantitative measurement of the radiation intensity is important in all cases, and the photolysis of uranyl oxalate offers a convenient and accurate chemical means for obtaining this quantity.

Suggestions for Further Work.—The absolute measurements of energy may be checked directly with a thermopile and standard lamp as given on page 401, using a cell with flat pyrex windows instead of the test tubes and suitable filters to absorb the light of wave length longer than 4,400 Å (page 395).

The experiment may be conducted with the lamp surrounded by double, *i.e.* concentric, tubes of pyrex of large diameter with a layer of solution to act as a filter. In this way several solutions may be selected to give filters for different wave lengths.

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68. The Photohydrolysis of Monochloroacetic Acid in Water

This experiment gives experience in the use of the actinometer, the calculation of quantum yields, and the application of potentiometric titrations. It requires a high-voltage quartz mercury-vapor lamp rich in light of 2,537 Å, but no optical instruments or quartz cells.

Theory.—Monochloroacetic acid hydrolyzes according to the reaction

$$CH_2ClCOOH + H_2O = CH_2OHCOOH + HCl$$
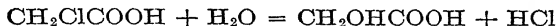
At room temperature the reaction is practically negligible, but when activated by ultraviolet light of 2,537 Å, which it absorbs, the reaction goes more rapidly. Not every molecule that absorbs a quantum of light undergoes reaction with the water because some lose their excess energy before they can react. On the average the chance of reaction is about one in three, giving a quantum yield of 0.31 at 25°. At 69° the quantum yield is 0.69.

This reaction is interesting historically in photochemistry because it was formerly and erroneously believed to be a good example of those few reactions in which the quantum yield is unity, *i.e.*, the primary photoactivation process is followed by complete reaction without complication by secondary reactions. In fact, it was used as an actinometer for obtaining quantum yields in other reactions. Some other early investigations also have reported quantum yields that were much too high, *e.g.*, the photolysis of acetone and the photosynthesis reaction by which carbon dioxide and water are combined by sunlight in the presence of chlorophyll in the living plant.

Apparatus.—High-voltage mercury-vapor lamp and transformer; four 5-cm crystallizing dishes; 50-ml pipette; two burettes; silver chloride electrode; voltmeter, rheostat; key; calomel cell and salt bridge (as described on pages 202 and 373); 500 ml solution $0.1M$ in uranyl sulfate and $0.01M$ in oxalic acid; 1,000 ml $0.01N$ potassium permanganate; 500 ml $0.1M$ monochloroacetic acid; 500 ml $0.005M$ silver nitrate.

Procedure.—The amount of monochloroacetic acid hydrolyzed is compared with the amount of uranyl oxalate decomposed under the same conditions of light absorption. The second reaction is used as an actinometer for calculating the quantum yield of the first. The monochloroacetic acid absorbs only the 2,537 Å light of the mercury-vapor lamp, but the uranyl oxalate absorbs the light up to 4,360 Å. Furthermore, the absorption coefficients for the two solutions are not equal. To meet these limitations a high-voltage "cold" lamp is used

in which more than 85 per cent of the light is at 2,537 Å* and the absorbing material is so concentrated that in the thickness used (2 cm) practically all the light entering the solution is absorbed.

In making up the solutions the oxalic acid is weighed out accurately so that it may be used to standardize the permanganate solution. The monochloroacetic acid need not be made up accurately because only the chloride ion produced by the reaction is determined. The four crystallizing dishes are set close together in a "clover leaf" and their positions marked. The lamp is mounted about 10 cm. directly over the dishes in such a position that each is illuminated equally. Filter papers soaked in a benzene solution of anthracene are convenient for finding by fluorescence the positions of equal illumination. To each of the four dishes is added with a pipette 50 ml of the uranyl oxalate solution, and the lamp is turned on.

A box with dull black walls (lined with black cloth or painted with lampblack in dilute shellac) is placed around the dishes and lamp to shield the ultraviolet light from the room. Special goggles must be used to protect the eyes.

After exposure to the ultraviolet light for an hour the contents of each dish is titrated with potassium permanganate after acidifying with dilute sulfuric acid and warming. Similar titrations are made on two 50 ml samples pipetted from the original solution, and the difference in titration between the original and the illuminated sample is a measure of the oxalic acid decomposed. If the solutions from the four different dishes do not show about the same decomposition within 5 or 10 per cent, the lamp is moved to give more uniform distribution.

In a second determination two of the dishes are filled with 50 ml of the uranyl oxalate solution, pipetted out, and the other two are filled with approximately 50 ml of the $0.1M$ monochloroacetic acid. All are exposed an hour to the ultraviolet light. The uranyl oxalate is titrated as before. The solutions of monochloroacetic acid are titrated for chloride ion, using $0.001M$ silver nitrate which has been standardized against a diluted standard solution of hydrochloric acid (or the silver nitrate is just weighed out accurately). The end point of the titration is determined potentiometrically, using a silver chloride electrode (page 374). The electrode may be made from a glass tube with a protruding platinum wire which is plated with silver as a cathode in a silver cyanide solution, and then as an anode in a chloride solution. The plating may be accomplished with a dry battery in just a few minutes.

* Such lamps for fluorescence studies are manufactured at about $50.

The silver chloride electrode is placed in the monochloroacetic acid solution from which an ammonium nitrate bridge leads to a calomel cell, and the potential is read on a voltmeter under conditions such that a minimum of current flows through the cell. This situation is effected as shown in Fig. 32 (page 202) with an inexpensive galvanometer and an opposing potential obtained from a dry cell and rheostat. When the silver nitrate is first introduced, the change in potential is slight because the silver is immediately precipitated, but at the end point the silver ions increase and there is a greater change in potential. It is necessary to make a blank test on the original monochloroacetic acid solution to allow for any chloride present as an impurity.

A second set of determinations is made with a longer exposure.

Calculations.—The number of molecules of oxalic acid decomposed (the number of moles $\times$ 6.02×10^{23}) is calculated from the difference in the permanganate titration. The number of quanta is calculated from the fact that one quantum decomposes 0.57 molecule of oxalic acid. The number of molecules of monochloroacetic acid hydrolyzed is calculated from the silver nitrate titration. This number divided by the number of quanta gives the quantum yield.

The number of quanta should be reduced by 15 per cent to allow for the fact that only 85 per cent of the light which is absorbed by the monochloroacetic acid is at 2,537 Å.

A better method for making this correction consists in making a determination with a flat quartz dish containing a concentrated solution of monochloroacetic acid, which absorbs the light of 2,537 Å, placed over the uranyl oxalate dish. In a second experiment the quartz dish contains water. The titration a obtained for uranyl oxalate with the monochloroacetic acid filter gives a measure of the number of quanta of wave length longer than 2,537 Å, and the titration b with the water gives a measure of all the radiation absorbed by uranyl oxalate together with a correction for losses of light from the filter due to reflection—amounting to about 4 per cent each at the air-quartz interface and at the air-acetic interface. If the titration obtained in the absence of a filter is denoted by c, the corrected titration for light of 2,537 Å alone is $\left(c - \frac{c}{b}\, a\right)$.

Practical Applications.—These experiments illustrate the use of the actinometer in measuring quantitatively the intensity of radiation and the determination of the efficiency of photochemical reactions.

Suggestions for Further Work.—Other photochemical reactions may be studied, using the uranyl oxalate solution as an actinometer.

The decomposition of malonic acid mixed with uranyl oxalate may be followed by titration with potassium permanganate.

The bleaching of dyes such as methylene blue or malachite green may be followed colorimetrically, using as standards various concentrations of the unbleached dyes.

The photobromination of toluene or tetrachloroethylene or other compounds may be studied. Oxidation reactions arising from dissolved air offer complications.

The photodecomposition of hydroiodic acid can be followed by titration with sodium thiosulfate, using starch as an indicator.

The photodecomposition of hydrogen peroxide may be followed by titration with potassium permanganate. This is a chain reaction subject to catalytic influences.

The lamp used in this experiment is suitable for studies of fluorescence in many organic and biological substances.

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69. The Photobromination of Cinnamic Acid

This experiment[*] involves quantitative measurements in photochemistry and experience in the use of a thermopile. It illustrates the study of chain reactions through the determination of quantum yields.

Theory.—The quantum theory gives the most satisfactory means of expressing the relation between the amount of light absorbed and the amount of chemical action produced. According to this theory, light is composed of units called photons, each containing a quantum of energy *e*. A quantum is the product of two factors, the frequency of the light ν and a universal constant h known as Planck's constant.

According to Einstein's relation there is a simple 1 to 1 relation between the number of molecules activated and the number of quanta absorbed. But usually there is no simple ratio between the number of molecules of product produced and the number of quanta absorbed, because reactions other than the primary process of light absorption are apt to take place also. The quantum yield is defined as the number of molecules of product resulting from the absorption of one quantum of energy.

If the quantum yield is less than unity, a reverse reaction, a competing reaction, or an internal loss of energy is indicated; if it is much larger than unity, a chain reaction is taking place in which the products of the first step are able to react with the original material liberating more of these products which go on giving more and more reaction.

The addition of bromine to cinnamic acid takes place rapidly in the light by means of a chain reaction. It is a favorable reaction for experimental study because the course of the reaction can be followed

by adding potassium iodide and titrating the amount of unreacted bromine with sodium thiosulfate.

The course of the reaction can probably be represented by the following equations:

$$Br_2 + h\nu \rightarrow 2Br \tag{1}$$

$$Br + C_6H_5CH{:}CHCOOH \rightarrow C_6H_5CHBr{\cdot}\overset{\cdot}{C}HCOOH \tag{2}$$

$$Br_2 + C_6H_5CHBr{\cdot}\overset{\cdot}{C}HCOH \rightarrow C_6H_5CHBr{\cdot}CHBrCOOH + Br \tag{3}$$
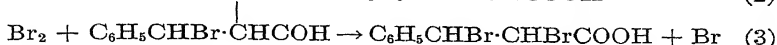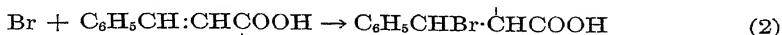
The bromine atom from equation (3) then enters another reaction like (2), and thus the reaction is continued by a "chain," until it is stopped by a reaction that destroys some of the chain carriers, such as the reaction

$$Br + C_6\overset{\cdot}{H}_5CHBr{\cdot}\overset{\cdot}{C}HCOOH \rightarrow C_6H_5CHBr{\cdot}CHBrCOOH \tag{4}$$

or

$$Br + Br \rightarrow Br_2 \tag{5}$$
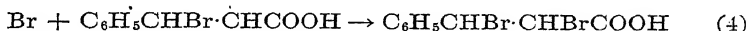
The free monobromo cinnamic acid radical $C_6H_5CHBr{\cdot}\overset{\cdot}{C}HCOOH$ has only a transitory existence. According to recent theories of chemical kinetics this molecule, containing a trivalent carbon atom, is short-lived not because it is unstable but because it is extremely reactive.

Actually the reaction is complicated by the pressure of dissolved oxygen from the air.

The addition of bromine to cinnamic acid takes place rapidly in the light by means of a chain reaction.

Apparatus.—A 500-watt lamp with concentrated filament; short-focus lens; two 50-ml flat-sided prescription bottles; rectangular glass vessel for constant-temperature water bath; glass cell containing copper sulfate solution; thermometer; 1-ml pipette; 5-ml pipette; 25-ml graduated cylinder; two burettes; 100 ml $0.01N$ iodine (dissolved with potassium iodide); 1 liter $0.01N$ sodium thiosulfate; starch solution; 100 ml 5 per cent potassium iodide; 100 ml $0.02M$ cinnamic acid, dissolved in carbon tetrachloride; 100 ml $0.01M$ bromine, dissolved in carbon tetrachloride; thermopile and galvanometer.

Procedure.—Light from a 500-watt projection lamp or an automobile headlight is rendered parallel with a convex lens of short focus. As shown in Fig. 56, it passes through a hole in a blackened metal sheet or cardboard, thence through the thermostat water, carbon tetrachloride solution, and onto the thermopile. A blackened cardboard strip with a suitable hole is placed in front of the thermopile to exclude scattered light. The thermostat is a rectangular glass vessel or a metal can with

glass windows.   It is fitted with a thermometer and hand stirrer and
kept at constant temperature within 1°.

The thermopile with a large single receiver may be constructed as
described on page 400.   It is connected directly to a low-resistance
galvanometer having a sensitivity of about 10^{-6} volt per millimeter.
The resistance of the thermopile and the critical damping resistance of
the galvanometer must be nearly equal.
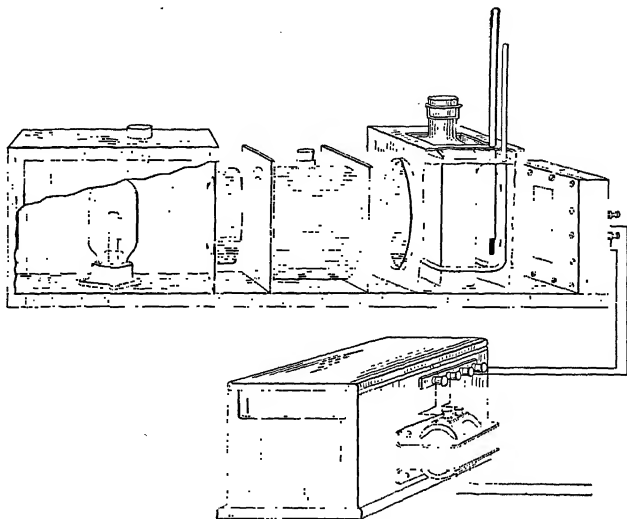
FIG. 56.—*Apparatus for measuring quantum yield in photochemical reactions.*

The zero reading of a thermopile and galvanometer is apt to drift on
account of temperature inequalities due to changing conditions in the
room.   Accordingly it is necessary to take frequent zero readings while
the light beam is blocked with a shutter of cardboard or sheet metal.
The difference between the galvanometer readings with the light on
and off is always taken as the thermopile reading.   Sometimes a
movable scale is used so that it may be slid along to make the zero on
the scale coincide with the galvanometer line when the thermopile is
shut off from the light.

A filter of nearly saturated solution of copper sulfate about 5 cm
thick in a rectangular glass cell or between cemented glass plates is
used to absorb the infrared and red light (page 396).

A prescription bottle with nearly flat sides is partly filled with carbon tetrachloride, and the light is turned on and focused so that all the beam that passes through the carbon tetrachloride is intercepted on the receiver of the thermopile. If the receiver is too small, the hole in the cardboard may be made smaller or the light may be focused down with a second lens. The galvanometer deflection should be near the maximum of the scale. If it does not cover the whole scale, a brighter light or a more sensitive galvanometer or thermopile is needed. If it goes beyond the scale, the size of the hole may be decreased or the current through the lamp may be decreased. If the galvanometer deflection is not constant, an ammeter is included in the lamp circuit and a rheostat is adjusted by hand as needed. After the proper adjustments have been made, the thermopile reading is recorded, *i.e.*, the galvanometer deflection when the light strikes the thermopile minus the deflection when the shutter is closed.

Stock solutions of about 100 ml are prepared of *approximately* $0.02M$ cinnamic acid in carbon tetrachloride and $0.01M$ bromine in carbon tetrachloride. One small drop of liquid bromine from a medicine dropper is usually sufficient. Operations with bromine should be carried out under the hood. The concentration of bromine should be such that about 10 to 20 per cent of the light passes through the solution in the cell.

In carrying out a photobromination, about 40 to 50 ml of each stock solution, measured in a graduated cylinder, is placed in the second prescription bottle, closed with a cork protected by tinfoil, and shaken. A couple of glass pearls or short rods improve the mixing. The bottle is placed in the thermostat at such a level that the beam of light will pass through near the bottom and samples can be removed from the top without reducing the area of solution exposed to the light.

A sample of exactly 5 ml of the solution is drawn into a pipette with the help of a rubber compression bulb and drained into an Erlenmeyer flask containing an excess of potassium iodide solution (10 ml of a 5 per cent solution). An excess of sodium thiosulfate is added, sufficient to bleach all the iodine, and the excess of thiosulfate is then titrated with the iodine solution, using starch as an indicator. The thiosulfate solution is standardized against a weighed quantity of potassium dichromate, which is added to potassium iodide solution and dilute sulfuric acid. The $0.01N$ iodine solution is then standardized against the thiosulfate.

The shutter is then opened, and the time and thermopile readings are recorded. The concentration of bromine should be such that 10 to 20 per cent of the light is transmitted as shown by a comparison of the

thermopile reading with that obtained with the pure carbon tetrachloride. The bottle is shaken by hand at frequent intervals to keep the concentration the same in the dark and light regions.

As the reaction continues the bromine combines with the cinnamic acid and the transmission of light increases. Three or four additional samples are removed for analysis during the course of the reaction until the bromine has nearly disappeared, the time and the thermopile reading being recorded for each sample. The height of the solution must not be lowered below the top of the light beam by the removal of the samples.

At the end of the determinations the thermopile reading is checked again, using the bottle of pure carbon tetrachloride.

As usual, a second determination is made.

The experiment requires carbon tetrachloride of good quality. If there is doubt concerning its purity, a test should be made with dilute bromine in carbon tetrachloride without any cinnamic acid. If the bromine fades out appreciably during a 10-min. exposure to the light, the carbon tetrachloride is unsatisfactory. Anhydrous calcium chloride in the stock bottle helps to keep the carbon tetrachloride dry.

The carbon tetrachloride from all the experiments is placed in a residue bottle for later recovery.

The galvanometer deflections are converted into absolute ergs per second of radiation falling on the thermopile, as described on page 401. This calibration value may be recorded on the thermopile. An *approximate* calibration may be made with a new 60-watt frosted Mazda lamp, mounted vertically with the socket below. The bulb is rotated so as to give the maximum deflection. Such a lamp when operating on the 110-volt line at a distance of 1 m gives direct radiation such that about 1.4 erg falls on 1 sq. mm per second, after passing through 1 mm of quartz in the thermopile window. Obviously, the lamps, the voltage, and the quartz vary, but this value is close enough to justify the calculations. The illuminated area of the thermopile receiver in square millimeters is multiplied by 1.4 and divided by the galvanometer deflection, to give the equivalent of one division of the galvanometer in terms of ergs per second.

Calculations.—The bromine titrations are converted into moles per liter, and these concentrations are plotted against the time. The number of moles of bromine made to disappear by the action of the light is then plotted against the time, due allowance being made for the actual volume of the solution in the flask after the withdrawal of the samples. The number of moles of bromine reacting photochemically in a given period of time (perhaps 5 min.) is then converted

into number of molecules for comparison with the number of quanta absorbed in the same time.

The difference between the thermopile readings with carbon tetrachloride alone and with a given bromine solution in the bottle is a measure of the radiation absorbed by the bromine. As usual, the thermopile reading refers to the observed scale reading minus the zero reading when the thermopile is darkened. The cinnamic acid is transparent to visible light. The average differences in scale divisions are multiplied by the number of ergs equivalent to one scale division and by the number of seconds of exposure in order to obtain the number of ergs absorbed by the solution in the given time interval. This value in ergs is then converted into number of quanta, with the help of the fundamental equation of the quantum theory

$$\epsilon = h\nu$$

where ϵ is the energy in ergs of one quantum, h is Planck's constant $(6.62 \times 10^{-27}$ erg second), and ν is the frequency of light. The average wave length may be assumed to be 5,000 Å, or 5×10^{-5} cm, and it may be converted into frequency by dividing into the velocity of light 3×10^{10} cm.

The quantum yield is calculated, *i.e.*, the number of molecules of bromine (Br_2) reacting per quantum of light absorbed. It should range from ten to hundreds, depending on the conditions. It is greatly affected by dissolved oxygen from the air.[3]

Practical Applications.—Several halogenations of organic compounds are influenced by light.

The study of photochemical reactions is frequently helpful in understanding ordinary thermal reactions. This is particularly true in the case of chain reactions, of which the photobromination of cinnamic acid is an example.

Photochemical reactions are very important in agricultural and many physiological processes.

Suggestions for Further Work.—The influence of concentration of bromine and of temperature may be studied further. A determination may be made at 15° instead of 25°.

The influence of oxygen concentration may be studied[3] by sweeping out the solution with nitrogen or carbon dioxide, and again with pure oxygen.

The reaction may be followed by the absorption of light, using the thermopile readings not *only* for energy measurements but for measurement of concentration.[2,3] A calibration curve is drawn with $\log I/I_0$ plotted against concentration of bromine, where I/I_0 is the per cent of light transmitted. According to Beer's law the line should be straight if the light is sufficiently monochromatic (page 59). The different concentrations may be made by diluting the concentrated solution with additions of carbon tetrachloride.

The experiment may be carried out with monochromatic light from a mercury lamp using filters.

References

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70. Photography

The theory and practice of photography is introduced in this experiment.

Theory.—In the development of photography, the art has been considerably ahead of the science. Recently, however, considerable progress has been made toward an understanding of the action of light on the photographic plate (or film).

A photographic plate (or film) has on its light-sensitive surface what is known as a photographic "emulsion," consisting essentially of a suspension of exceedingly fine grains of silver bromide in gelatin. These grains of silver bromide have been sensitized in the process of manufacture of the emulsion, either by heating the emulsion or by treating it with a small amount of ammonia. Sometimes these two processes are combined in one. The ordinary photographic paper for making prints by contact printing has a similar emulsion on its surface, except that silver chloride is the sensitive material. Enlargements are usually made on a bromide paper, however, as bromide emulsions are much faster. Fast chloride emulsions are sometimes used. They are intermediate in speed between the bromide and the ordinary chloride papers.

When sensitized grains of silver halide are exposed to light in the presence of gelatin, they are activated in such a way that they are more easily reduced to silver by a suitable mild reducing agent. The effect produced by the action of light is called the "latent image." Nuclei are produced in the silver halide lattice by the light, and when the plate is developed, each grain containing a nucleus is reduced to silver. The silver halide grains that do not contain nuclei are reduced only after a much longer period of development, a sort of "inoculation" from the already developed grains apparently being necessary for their reduction. The production of nuclei seems to be dependent upon the presence of traces of sulfur in the emulsion.

After development the plate is fixed. In this process the unreduced grains of silver halide are dissolved in sodium thiosulfate (hypo), leaving black, reduced grains of silver. The parts that were brightest when the plate was exposed become the darkest when the plate is developed, and the finished plate is called a "negative." The intensity of the silver deposit produced in each area on the plate must be in direct

proportion to the intensity of the reflected light from the corresponding area in the object being photographed; otherwise, a true representation of light and shadows will not be obtained. After fixation is complete, the plate is washed and thoroughly dried. A photographic printing paper is then placed behind and firmly in contact with the negative (in a printing frame) and exposed to light; the development and fixing described above are repeated on the paper. The lightest spots on this print correspond to the darkest spots on the negative and to the lightest parts of the original.

The camera and lens are devices for projecting upon the plate an image of the object to be photographed, and the shutter regulates the time of exposure. The shutter is also provided with an adjustable diaphragm to control the amount of light admitted.

The amount of change produced on the plate by the action of the light is, of course, dependent upon the amount of light energy acting. Obviously, the same amount of light can be admitted through the lens by using (a) a small aperture and long exposure, or (b) a large aperture and short exposure. Better definition and greater depth of focus are obtained by the use of a small aperture. In portrait work, however, great depth of focus is not desired; hence a large aperture should be used. In photographing landscapes, it is best to "stop down," as far as light conditions permit, for the longest exposure

G. 57.—Characteristic curve for the exposure of a photographic plate.

practicable, *viz.*, 0.04 sec., if the camera is held in the hand. In photographing rapidly moving objects, an exposure of 0.01, 0.002, or even 0.001 sec. may be necessary, but such exposures (necessitating large diaphragm apertures) result in a loss of definition and depth of focus.

In a perfect negative, *i.e.*, one which has silver deposits in the various areas proportional in amount to the intensities of light reflected from the corresponding areas of the objects being photographed, the densities of the deposit are proportional to the logarithm of the corresponding exposure. If a series of identical plates are given exposures increasing in geometrical progression (so that their logarithms increase in arithmetical progression), and all plates are subjected to exactly the same process of development, the curve showing the relation between the logarithm of exposure and density of silver deposit will have a form

like that shown in Fig. 57. This characteristic curve is of the same general form for every plate and developer. In the first section (I) the density of the deposit increases *faster* than the condition of perfection requires. This represents underexposure and a contrasty, harsh picture results. In the third section (III) the deposit of silver increases more *slowly* than the law of perfection requires. This represents overexposure, and the resulting prints will be flat and lacking in detail. Only in the straight-line portion of the curve (II) do we find the law followed strictly; hence any exposure falling on this portion of the curve is a correct exposure, *i.e.*, the ratio of the deposits of silver corresponds to the light intensities in the object being photographed. Prints made from negatives that have been given any exposure falling on this straight portion of the curve will be undistinguishable from each other, although the negatives with the longer exposures, naturally, will have greater average densities and will require longer printing. The ratio of densities in the different parts of the negative remains the same, however.

The longer the straight section in the curve, the greater is the latitude of the plate, *i.e.*, the more the exposure can be varied without altering the ratio of silver deposits in the various areas. Obviously, it is best to use plates that have great latitude, as then the length of exposure need not be determined so exactly. Inasmuch as slow plates usually have more latitude than do fast ones, it is a good rule to use the slower plates when high speed is not absolutely required. The slower plates usually have a finer grain than do the fast ones, and this is of particular advantage in the making of enlargements from small negatives and in making lantern slides, which are greatly magnified on projection. If a coarse-grained plate is used, the grains will show upon enlargement. The grain size can be controlled somewhat by the use of special developing solutions.

Apparatus.—Camera; plates; plateholder; electric lights; focusing cloth; exposure meter; developer; fixer; photographic paper; dark room with red light.

For students who have had no experience in photography the taking of a line drawing is suggested. For students who have developed their own films, the making of an enlargement will prove interesting.

Procedure.—If a line drawing is to be copied by photography, it is held securely in a vertical position, squarely in front of the camera, and illuminated evenly by two 200-watt frosted lamps backed by white reflectors. Care must be taken that the position of the lights is such that no reflected glare enters the lens. The camera is moved forward or backward until the image is of the right size to fit the plate, and the

lens is focused until the image stands out sharply on the ground glass in the back of the camera. A hand lens is useful in getting the exact focus.

The plateholder is loaded in the dark room with two plates (4 by 5 in.), using only a weak, red light. The emulsion or dull side is arranged to face the lens. If the plate is smaller than the plateholder, the latter is fitted with a nest of adapters. If a cut film is used, it is slipped into a film sheath and this is then placed in the holder as if it were a plate. It is necessary to have contrast in a photograph of this kind, and a process plate is used. If it is desired to take a photograph of an ordinary object, a plate of normal contrast is used. The length of exposure may be determined with an exposure meter. The Weston (or other) photoelectric exposure meter is the most satisfactory type, inasmuch as the light intensity is measured by a photoelectric cell. The meter should be held near the object to be photographed as it is only the light reflected from the object that is to be measured. A good rule is to hold the meter at a distance approximately equal to the diagonal of the area to be photographed. Light from extraneous bright objects, or the sky, is thus excluded. The correct length of exposure is a function of the light intensity, the area of the diaphragm opening, and the type of plate. Process plates require about six times the exposure of an ordinary plate, as given on the exposure meter. The instrument must be set for the particular plate or film being used, as the sensitiveness of photographic materials differs greatly. To use the Weston meter, for example, one must know the speed of the film or plate in terms of the Weston scale. Speeds stated in terms of other scales (Scheiner, H and D, etc.) can be converted to the Weston scale.* The diaphragm openings in the camera shutter have different values, depending on the system used, U.S.† or f. At a setting of 16, the two

FILM SPEED COMPARISON TABLE

American Scheiner	American H and D	Weston 1938	American Scheiner	American H and D	Weston 1938
5	20	0.8	20	640	26
8	40	1.6	23	1,250	50
11	80	3.2	26	2,500	100
14	170	6.8	29	5,000	200
17	320	13.	32	10,000	400

† The abbreviation U.S. stands for uniform system. In this system, each succeeding opening is half the area of the preceding one. See Neblette.[3]

systems have identical areas of diaphragm opening (also U.S. $8 = f{:}11$, and U.S. $32 = f{:}22$). In the f system, the diaphragm opening represented by $f{:}16$ means that the diameter of the opening is one-sixteenth of the focal length of the lens. With the setting of $f{:}16$ and a process plate, an exposure of about 10 sec. or less is given on the reading of the exposure meter. Two pictures are taken with different lengths of exposure.

After the camera has been focused, using the largest opening of the diaphragm, the loaded plateholder is inserted in the back of the camera, without changing the position of the camera. The shutter is closed, the diaphragm is adjusted to the desired opening, and the slide is pulled out of the plateholder. After exposure, the slide is immediately replaced. It is a convention that the black side of the handle on the slide is placed outward, after the plate has been exposed.

Three trays containing developer, water, and fixing bath are placed near the red lamp. At 20°C., the image appears in 15 to 20 sec., but development should be continued until the details in the shadows are brought out, usually requiring about 3 min. Control of temperature is very important, as a few degrees of change greatly influence the action of the developer. The proper point at which development should be stopped must be learned by experience. The plate is then rinsed to remove alkali and placed in the fixing bath for about 20 min., or at least 5 min. after all the halide (white) is apparently removed from the plate. This rinsing of the plate is important, especially in warm weather, for tiny "blisters" are likely to form, owing to too rapid a liberation of carbon dioxide in the acid fixing bath. After fixing, the plate is washed for at least half an hour in running water, placed on a rack, and allowed to dry. Upon completion of washing, the surface of the wet plate should be swabbed off (lightly) with wet absorbent cotton before drying. This removes any possible sediment that may have collected on the gelatin surface.

The dry negative is set in a printing frame, a piece of printing paper is placed face down on the negative, the frame is closed and exposed for a few seconds to an electric light, at a suitable distance, *e.g.*, 2 ft. Ordinary Velox or Azo F4 or other contrast paper is used, because the greatest possible contrast is desired. For portraits or landscapes one would use a "softer" paper, *i.e.*, one giving less contrast. Inasmuch as the emulsion on printing papers is much less sensitive than that on plates or films, a yellow light may be used to illuminate the dark room.* To ascertain the proper printing time, a strip of paper is given a set of preliminary exposures, each succeeding exposure being double the

* The Eastman OA filter is even better. It can also be used for bromide papers and lantern-slide plates.

preceding one. By development of this strip, the proper length of exposure is quickly determined. A properly exposed print takes 60 to 90 sec. to develop. Development should not be too prolonged (forced), nor should it be necessary to remove the print quickly to save it. Best results are obtained by full development of a properly timed printing. As soon as the print has acquired the desired intensity, it is rinsed in a dilute acetic acid solution (5 per cent). This rinsing neutralizes the alkali and stops development, and greatly reduces the tendency of the print to stain in the fixing solution. While in the fixing solution, the prints should be moved frequently. Complete removal of the fixing solution is important. This can readily be ascertained by allowing the drippings from the wet prints to drop into a dilute alkaline permanganate solution. If no discoloration is produced, the hypo has been removed.

The following developer* is recommended for process or contrasty plates. Equal parts of A and B are mixed just before using.

A		B	
Water....................	100 ml	Water..................	100 ml
Hydroquinone.............	2.5 g	NaOH..................	4 g
Na₂SO₃....................	2.5 g		
KBr......................	2.5 g		

The following developer is good for general use with ordinary plates, and is very easily prepared.

> 1 g pyrogallic acid   120 ml distilled water
> To this solution are added 20 ml of a saturated solution of sodium sulfite (pure) and 15 ml of a saturated solution of sodium carbonate. It is convenient to have a wooden mustard spoon trimmed to such size that it will hold 1 g of pyrogallic acid when filled level full, thus saving the time necessary for weighing.

The following developer is recommended for Azo or Velox prints. For Special Velox, the solution is diluted with an equal volume of water:

Water...	300 ml
Metol (or elon)†....................................	0.5 g
Hydroquinone.......................................	2.0 g
Na₂SO₃..	7.0 g
Na₂CO₃..	13 g
KBr (10 per cent)...................................	2 ml

* Although the formulas given here have been found satisfactory, it is recommended that the formulas specified by the manufacturer for the particular plate, film, or paper be used if much work is to be done.

† Trade names for monomethyl-p-aminophenol sulfate.

The following solution is recommended for fixing plates or prints:

Solution *A*

Water..	500 ml
"Hypo" ($Na_2S_2O_3 \cdot 5H_2O$, crude)......................	125 g

The water may be heated to dissolve the hypo quickly, but it must be cooled before solution *B* is added.

A hardening solution, *B*, is prepared by dissolving in 75 ml of water, 10 g of glacial acetic acid, 10.5 g of powdered alum, and 10.5 g of sodium sulfite. The reagents are added in the order given, and when fully dissolved, the hardening solution *B* is poured into the thiosulfate solution *A* slowly, with stirring. The hypo must be *fully* dissolved before adding the hardener, otherwise sulfur will be deposited. The hypo solution must not be hot, else sulfur will be deposited.

Instead of taking a photograph of a drawing it may be more interesting to make lantern slides, or enlargements.

In making *lantern slides*, the negative should be made on a lantern-slide plate. These plates are less sensitive than ordinary plates, consequently a much stronger red light can be used in the dark room. They come in several grades of contrast (soft, medium, and contrast). For a line drawing a contrast plate is used. The printing is done just as in printing on paper, except that the exposure is much shorter. For a negative of medium density, an exposure of 1 to 2 sec. at a distance of 30 in. from a 25-watt tungsten lamp is suggested. Lantern slides are much improved in brilliancy by brief immersion (15 to 30 sec.) in a dilute (0.2 per cent) solution of potassium ferricyanide, after removal from the fixing solution and before washing. Any slight fog in the "high lights" (clear areas) is thus removed. This clearing procedure is also recommended for making negatives of line drawings. Resulting prints will be more brilliant.

The following developer is recommended for lantern slides:

Water (about 125°F.) (52°C.)........................	500.0 ml
Elon...	1.0 g
Sodium sulphite, desiccated (Eastman Kodak Company).	75.0 g
Hydroquinone......................................	9.0 g
Sodium carbonate, desiccated (Eastman Kodak Company)	25.0 g
Potassium bromide.................................	5.0 g
Cold water to make................................	1.0 l.

The chemicals are dissolved in the order given.

Development is carried out in a tray for 5 min. After development, the slide is rinsed for about 10 sec. in running water and fixed 10 to 15 min. in the standard acid-hardening fixing bath.

Enlargements are made with the enlarging camera. Any fairly contrasty negative may be used. Very flat negatives do not give good

enlargements. A 200-watt lamp and a condensing lens may be used as a source of light. If no suitable condensing lens is at hand, a frosted bulb may be used, interposing a sheet of opal glass between the bulb and the negative. By suitable adjustment of the bulb and opal glass, even illumination can be obtained. The correct time of exposure must be determined by experiments with a small strip of the paper.

Various printing papers are available. The glossy-surfaced papers, such as Press Bromide, are suitable for photographs of line drawings and apparatus. Prints on such paper are allowed to dry on ferrotype plates. The prints are laid face down on the highly polished plate, and the excess of water is removed by blotting and rolling the print into intimate contact with the plate. In order to prevent prints from sticking, the plate must be thoroughly clean. It should frequently be rubbed with a clean cloth, having on its surface a few drops of 3-in-1 oil, or a few drops of a dilute solution of paraffin in benzene. The plate must then be rubbed with a clean cloth, until apparently free from oiliness.

The following developer is recommended for enlargements:

Distilled water (50°C.)	500 ml
Metol (or elon)	0.8 g
Na_2SO_3 (anhydrous)	11.3 g
Hydroquinone	3.2 g
Na_2CO_3 (anhydrous)	7.5 g
KBr (10 per cent)	4.0 ml
Water to	1.0 liter

This solution is diluted with an equal volume of water for use. Development should require about 90 sec. at 20°C. for properly exposed prints.

Calculations.—The function of each of the ingredients in the developers and the fixing bath is to be explained. A brief discussion of the camera and lens should be included also.

Practical Applications.—The practical applications of photography are too many to be enumerated.[2-4] Many operations in physical chemistry depend on photographic methods, such as spectrophotometry.

Suggestions for Further Work.—Photographs of objects as well as line drawings may be taken, *e.g.*, a laboratory apparatus setup.

Photomicrographs are made by inserting the top of the microscope into the lens holder of the camera with a special light-tight adapter. The microscope is focused so that the image on the ground glass is sharp. A small magnifying glass should be used in this operation; it is used to best advantage on a clear glass instead of a ground glass. It is often convenient to have a large microscope cover glass cemented on the ground side of the ground glass to give a transparent area for focusing with a lens. A 200-watt lamp may be used as a source of light, and a

screen of ground glass placed near the object helps to make the illumination uniform. Special effects may be obtained by staining the slide and using color filters. Specially sensitized plates are necessary when stains are used. These are useful in photographing colored objects. They are known as "panchromatic plates," and must be developed in complete darkness, as must also the specially sensitized plates used in spectroscopy.

References

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3. NEBLETTE, "Photography, Its Principles and Practice," 2d ed., D. Van Nostrand Company, Inc., New York (1930).
4. MATTHEWS and CRABTREE, Photography as a Recording Medium for Scientific Work, *J. Chem. Ed.*, **4**, 9 (1927).
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71. Spectrography

The value of spectroscopy in theoretical chemistry and in practical analysis is stressed in this experiment, and opportunity is given for the study of the photographic process.

Theory.—The spectroscope and its applications are discussed on page 39. The spectrograph is simply a spectroscope in which the photographic plate is substituted for the eye. A permanent record of a large section of the spectrum is obtained quickly and easily with a single exposure. The spectrophotometer which measures directly the intensity of transmitted light at different wave lengths is described on pages 64 and 58. The photographic process is discussed on page 286.

Apparatus.—Spectrograph; plateholder; photographic films including panchromatic film;* mercury-vapor lamp; iron arc; graphite arc; hydrogen tube; nitrogen dioxide; potassium permanganate.

Procedure.—Panchromatic films or plates are necessary for use with red and yellow light, and they must be handled and developed in complete darkness. The loading of the filmholder is described on page 289 except that no light is used. The emulsion side is somewhat rougher; it can be identified by rubbing the finger lightly along the edge of the film on both sides or by small V cuts on the edge. The emulsion side is placed outward in the holder.

The focusing of the spectrograph is carried out with a ground-glass plate in the position of the plateholder. The adjustment will be slightly different in different parts of the spectrum, and the sharpest

* It is best to use the special plates made for spectrographic work.

focus is obtained for the center of the plate. The focusing knob is turned until the lines, which are images of the entrance slit, are sharp and bright. The entrance slit is adjusted to give a narrow line, but it should not be so narrow as to require an inconveniently long exposure, or so narrow as to exclude some of the weaker lines.

The slit is then covered with a shutter, the holder containing the film or plate is attached to the spectrograph and its black cover is withdrawn. The holder can be moved up or down by means of a rack and pinion so as to take several exposures on a single film. The knob is turned until the top edge of the film is in position for the first exposure.

If the instrument is provided with a reference scale for labeling the spectra, an electric light is held in position for a few seconds to produce an image of the scale at the top of the film.

Next the shutter in front of the slit is removed, and a spectrum of the mercury arc is taken, using an exposure of 1 or 2 sec. Any mercury-vapor lamp may be used, care being taken to shield the eyes from ultraviolet light by using goggles. The capillary lamps that screw into a lamp socket such as the General Electric H4 are satisfactory and inexpensive. An inexpensive transformer is required.

Several exposures are made of different spectra on the same film, moving the film holder up about 1 cm for each successive exposure. Careful notes are taken on the spectrum used, the time of exposure, and the slit width. There will be nothing except these notes to designate the different spectra on the finished plate.

The times of exposure must be learned by experience for the different sources of light; in general they run from a few seconds to a few minutes. Two or three different exposures varying greatly in time may be taken first as a guide to better timing for a second film, or approximate exposure time for a given lamp and slit width may be written down on a tag attached to the spectrograph.

Some of the following spectra may be photographed.

1. Mercury arc in quartz or pyrex lamp.

2. Hydrogen or helium discharge in a Geissler tube excited with an induction coil.

3. Neon glow lamp.

4. Iron arc from two rods or nails in insulated clamps, using a suitable resistance (20 to 50 ohms) in series on the 110 volt a-c or d-c line.

5. Graphite electrodes and arrangement similar to No. 4. On the lower electrode may be placed samples of various alloys or other materials which may be analyzed by means of the characteristic spectra.

6. Absorption spectra of 0.01 per cent potassium permanganate solution at varying dilutions.   For example, one volume of this 0.01 per cent solution is diluted with water to give the following volumes: 1, 2, 8, 32, and 128.

7. Absorption spectra of didymium glass.

8. Absorption spectrum of nitrogen dioxide at low pressure in a sealed tube.

The absorption spectra of liquids are made with a 25-watt lamp and an absorption cell with polished windows interposed in front of the slit.   Gases are sealed off in glass tubes with thin, smooth blown ends.

In accurate work the scale or a reference spectrum, such as mercury or iron, is used as the first and last exposure on the film.   A straight line drawn from a scale marking at the top to the same mark at the bottom will give accurately the position of a line in any of the spectra, and if there has been any slippage of the film holder the fact is readily detected.

After all the exposures have been taken, the cover is replaced and the holder taken to the dark room where the film is developed in total darkness.   The formula and time of development of one developer (D76) for panchromatic films is given here.   Others recommended by the manufacturers may be used equally well.

Distilled water 52°C. (125°F.)	375 ml
Elon	1 g
Sodium sulfite (desiccated)	50 g
Hydroquinone	2.5 g
Borax	1 g

This solution is diluted with cool distilled water to give 500 ml.

The film is developed for 17 min. at 18.5°C. (65°F.), or for 13 min. at 22°, the temperature being regulated to 1°, using a piece of ice if necessary.

The film is rinsed and fixed in a "hypo" bath containing 125 g of sodium thiosulfate in 500 ml of water, as described on page 292.   After fixing for several minutes until all traces of white silver halide are removed, the film is rinsed for an hour in cold running water and dried.

Usually the films are interpreted directly without making a positive print.

Calculations.—The spectrograph is calibrated in a manner similar to that described on page 39, using the mercury spectrum and plotting wave lengths against the linear distance in millimeters measured accurately along the film, starting with a distinctive reference line or scale reading at the extreme short wave length end of the spectrum.

The different lines in the mercury spectrum are identified from the spectrum given on page 392, and the corresponding wave lengths in angstroms are plotted for each line. A smooth curve is then drawn through the points, and the wave length of any new line is determined by interpolating its distance in millimeters on this graph.

The principal emission lines and absorption bands of the different spectra are identified and recorded.

The Balmer lines in the hydrogen or helium spectra are identified, their wave lengths determined and compared with the theoretical values as calculated with the help of the Rydberg constant (page 43).

If any unknown materials are examined, they are identified through their spectral lines.

Practical Applications.—Applications are discussed on page 43. The photographic recording of spectra has greatly increased the speed and accuracy of spectroscopy.

The spectrograph is widely used in practical qualitative and quantitative analysis.

The nature of the absorption spectrum, whether continuous or discontinuous, is of value in interpreting the mechanism of the molecular absorption and the nature of certain photochemical reactions.

The intensity of transmitted light at the different wave lengths is often desired. It can be obtained by measuring the opacity of the lines on the photographic film with a photoelectric cell or thermopile. Another more common procedure involves splitting the beam of light into two parts giving two matched spectra, one directly above the other. One beam passes through the absorbing material, and the other is reduced in intensity by measured amounts by means of a moving sector wheel, a Nicol prism, or a wedge of partly opaque glass. The positions of equal darkness on the two spectra are marked on the film. Several exposures are made on the film at different intensities, and a line connecting these points of equal opacity gives a good measure of the absorption band.

The extent of the absorption between the maxima of the absorption bands can be obtained also by taking several exposures and varying the time, the concentration, or the thickness. These methods are less satisfactory than the split-beam method, and all depend on a close relation between blackness of photographic plate and intensity of light. The electrical method of measuring light intensity directly without the medium of the photographic plate as described for the photoelectric colorimeter (page 58) and spectrophotometer (page 64) is usually better than the photographic method for absorption spectra.

In using the emission spectra for quantitative work it is necessary to calibrate the spectral plates with known amounts of material in the arc or spark under the same working conditions.

The spectrograph is essential for spectral work in the ultraviolet.

Suggestions for Further Work.—The spectra of many different colored substances may be taken and the absorption bands located. Unknowns may be identified and quantities of material estimated empirically by the emission spectra. The procedures described on pages 42 and 66 may be followed.

Absorption spectra can often be used in determining the molecular structure of organic compounds.   The change in the position of an absorption band as influenced by substituting different groups in the molecule may be studied.

References

Many of the references on pages 43 and 67 are applicable to this experiment.

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2. BRODE, "Chemical Spectroscopy," John Wiley & Sons, Inc., New York (1939).
3. "Optical Methods in Control and Research Laboratories," Adam Hilger, Ltd., London (1923).
4. BALY, "Spectroscopy," Longmans Green & Company, London (1927).

72. The Raman Spectrum

A Raman spectrum is taken with a long exposure with a spectrograph using a mercury-vapor lamp.   The position of the Raman lines is measured, and the corresponding infrared lines are calculated.

Theory.—In 1928 Raman found that when monochromatic light is passed into a transparent material some of the scattered light has a wave length slightly different from that of the original light.   Theory had predicted this effect, but no one previously had made long enough exposures under carefully controlled conditions to find it.   The photon of radiation interacts with a molecule, and the energy of one increases and that of the other decreases.   The energy transfer is "quantized," and the definite small units that the molecule can take up or give off correspond to definite bands in the infrared absorption spectrum which in turn correspond to definite displacements of the atoms in the molecule.   The fundamental equations are

$$\epsilon_{incident} = \epsilon_{Raman} \pm \epsilon_{molecular\ energy}$$

and

$$h\nu_{incident} = h\nu_{Raman} \pm h\nu_{infrared}$$

where ϵ is a quantum of energy, h is Planck's constant 6.62×10^{-27}, and ν is the frequency of light.   The small difference in frequency between the incident light and the frequency of the scattered light then is equal to the infrared frequency which corresponds to a change in the energy of the molecule.

Since the molecule can receive or give out energy, the Raman spectral line may have either a longer or a shorter wave length. There may be several lines corresponding to different energy levels in the molecule and different infrared bands.   By carefully measuring the position of the Raman lines, which appear on the spectrogram as weak lines at the side of the exciting line of the incident light, it is

possible to calculate the frequency and wave length of the infrared lines.

The infrared lines can often be determined more easily from Raman spectra than from direct absorption measurements in the infrared, and when a solvent that is opaque in the infrared is used, the indirect method of the Raman spectrum is the only method available. Sometimes a Raman line is missing from an infrared spectrum, and sometimes an infrared line is missing from a Raman spectrum. Under these conditions, conclusions can be drawn regarding the quantum restrictions in the excited and the unexcited molecules.

Apparatus.—Spectrograph; mercury-vapor lamp; glass tube with window at end; carbon tetrachloride.

Procedure.—A spectrograph of fairly large aperture and an intense source of light are necessary, as otherwise impractically long exposures are necessary. High dispersion is not so important in the spectrograph.

The liquid to be examined is contained in a tube about 2 cm in diameter and 15 cm long. It has a window at one end, and the other end is drawn down to about 1 cm diameter and bent upward so that the whole horizontal tube may be readily filled. The window end is a bulb of thin glass blown out uniformly, and it is placed 1 or 2 cm from the slit of the spectrograph and pointing directly toward it. The opposite end is painted black.

The tube is filled with carbon tetrachloride. The mercury-vapor lamp is placed alongside of the tube and as close as convenient without overheating.

For some compounds monochromatic light is necessary, and filters are used. A mirror or a curved sheet of aluminum on the other side of the tube helps to conserve some of the light.

Any mercury-vapor lamp rich in the 4,357 line can be used provided that it is sufficiently intense and carries several hundred watts.

A Raman exposure of 2 or 3 hr. is taken, and just afterward an exposure of a fraction of a second and one of several seconds are taken with the mercury lamp alone for reference. In these exposures the tube of carbon tetrachloride is removed.

The uses of the spectrograph are described on page 43.

Calculations.—The Raman lines, which do not appear on the simple spectrum of the mercury lamp, may be seen faintly at the side of the 4,357 Å line. As some of these lines are hard to see, the film is turned in various directions and the illumination changed in an attempt to bring them all out.

The distance between the centers of the 4,357 Å and the 4,047 Å lines is carefully measured with a millimeter scale or micrometer gage, and the number of angstroms per millimeter in this part of the spectrum is calculated on the approximate assumption that the relation over this small range is linear. The distance from the 4,357 Å line to each of these Raman lines is measured and expressed in terms of angstroms. These differences are then converted into wave numbers and recorded for each of the lines. These wave numbers, expressed as differences from the exciting lines, are actually the wave numbers of the infrared lines.

They are compared with the recorded values for the infrared spectra of carbon tetrachloride.[1]

Practical Applications.—Many uses have been found for the Raman spectra described in the voluminous literature published since the effect was discovered in 1928. Spectral lines in the infrared are used in theoretical calculations of internal energies of molecules, specific heats and entropies, equilibrium constants and reaction rates. The structure of molecules can be deduced from the modes of vibration, which in turn are obtained with the help of the infrared spectra. Aside from these quantitative calculations, many interesting chemical effects of a more qualitative nature can be readily obtained. For example, the formation of a compound between two liquids can be determined from the appearance of a new Raman line. The change in ionization as a function of the dilution may be determined as in the case of nitric acid and water or zinc nitrate and water.

Suggestions for Further Work.—The Raman spectra of other liquids may be determined. Stannic chloride, or chloroform or zinc nitrate in water are suggested.

References

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4. HIBBEN, Chemical Applications of Raman Effect, *J. Chem. Phys.*, **5,** 706, 710 (1937).

PART II
APPARATUS

CHAPTER XVI

PHYSICAL PROPERTIES OF GASES

Density

The molecular weight of a gaseous substance can be determined by weighing a known volume of the gas and calculating the weight of 22.4 liters at 0°C. and 760 mm pressure. Several methods have been devised for this purpose.

Dumas Method.—In this method a glass balloon (250 to 300 ml) is filled with vapor, under atmospheric pressure and at a known temperature, and the weight of the vapor is determined. The precautions used in weighing mentioned for the Regnault method (page 3) are equally necessary here.

About 5 ml of the liquid is placed in the clean, dried, weighed glass balloon, and the balloon is immersed in some liquid, usually water, which can be heated to at least 20° above the boiling point of the substance to be vaporized. The balloon must be immersed nearly to the constricted tube where it is to be sealed off. As soon as the liquid in the balloon has completely evaporated, the temperature of the bath is noted, and the tip of the balloon is quickly sealed off with a small blast lamp, the sealed-off piece of glass being saved for weighing. The barometer is then read, the balloon is cooled to room temperature, and its contents weighed. A counterpoise is used in all weighings. The volume of the balloon is now determined by breaking off the tip under air-free water at a measured temperature and allowing the vessel to fill. The broken-off pieces are saved for weighing. If a gas bubble is left after the water-soluble vapor dissolves, it is evident that the quantity of liquid vaporized has not been sufficient to sweep out all the air.

Although a correction might be attempted, such a correction is uncertain. In general, the best way to "make a correction" is to avoid the necessity for making the correction through improvements in technique. The weight of the water in the water-filled balloon, with the known density, gives the volume of the vessel at room temperature, but not at the temperature at which it was sealed. If the cubical expansion of glass is known, this difference is easily calculated.[1] It

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[1] The expansion of pyrex glass is given by BUFFINGTON and LATIMER, *J. Am. Chem. Soc.*, **48**, 2305 (1926).

is necessary to correct for the buoyancy of the air when the balloon is sealed off, but not when it is open and filled with air.   Knowing the volume of the vessel and the density of air at the prevailing temperature and atmospheric pressure, this calculation is simple.

Hofman Method.—The Hofman method is perhaps the simplest in principle, although it is not often used.   The apparatus is essentially a steam-jacketed barometer tube with the upper part of the tube calibrated in cubic centimeters and in millimeters.   A pyrex tube, 1.5 cm in diameter and 100 cm long, sealed at one end, is filled with boiled-out mercury and then inverted and placed vertically over a dish of mercury. The mercury stands at atmospheric pressure with the Toricellian vacuum above it.   A larger tube surrounds the inner tube and dips below the surface of the mercury in the open dish.   Steam or other vapor is passed through this jacket at a measured temperature.   A side tube near the bottom permits condensed liquid to run out.

The liquid is weighed out into a small tube with a capillary neck and is inserted below the open end of the central tube.   The small tube must be completely full; otherwise, air will be introduced.   The tube rises to the top of the mercury and the liquid vaporizes into the Toricellian vacuum above it.

The mercury column falls, and when steady conditions are reached, the volume of vapor and height of the mercury column are read directly on the tube.   The thermometer suspended in the vapor in the outer tube gives the temperature, and the pressure is obtained by subtracting the height of the mercury column from the original barometer reading. The height of the mercury column is corrected to 0° (allowance also being made for the weight of the glass bulb), and a correction is made for the vapor pressure of the mercury.

Lumsden Method.—The Lumsden method[1] is similar to the Victor Meyer method, except that the increase in pressure is measured rather than the increase in volume.   A mercury manometer is used, and there are no uncertain corrections for the pressure of water vapor.

Measurement of Volume

Displacement Method.—A measured quantity of gas may be introduced into a system by displacing it with a measured quantity of liquid, in a flask provided with a two-holed rubber stopper.   In an alternative method, the gas may be drawn over by running out a measured volume of liquid.   The gas must be insoluble in the liquid.   Mercury is the best liquid for most purposes, but it is too heavy for large volumes, and

[1] LUMSDEN, *J. Chem. Soc.*, **83**, 342 (1903).

water, oil, nitrobenzene, and sulfuric acid have been used. Most of these liquids have a negligible vapor pressure, but a correction is necessary in the case of water. The temperature of the incoming liquid must be the same as that of the vessel.

Large volumes of gas are measured conveniently with commercial gas meters, in which cups or vanes rotate in a tight chamber containing a liquid at the bottom. The number of revolutions is recorded on one or more circular scales. The meters are calibrated with known volumes of gas.
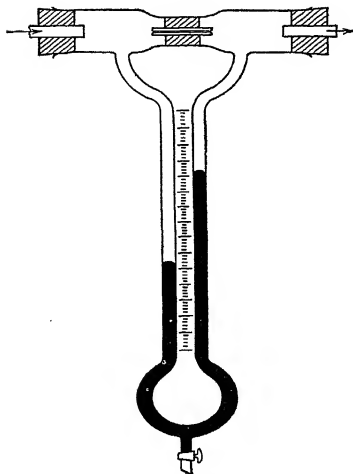
Gas may be stored conveniently in a bottle filled with liquid and connected to an empty bottle at a higher level in such a way that the liquid is forced into the upper reservoir by the incom-

Fig. 58.—Flow meter.

Difference in heights
of manometer readings
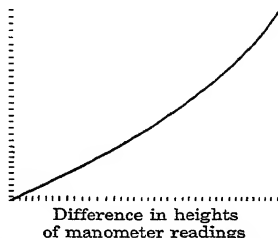
Fig. 59.—Calibration curve for
flow meter.

ing gas. The ordinary gas tank, with inverted cylinder floating in water, is convenient for large quantities of gas.

Flow Meters.—The rate of flow of a gas is conveniently measured with a flow meter, as illustrated in Fig. 58. The difference in pressure on the two sides of a capillary tube, as indicated by the manometer, is a measure of the rate of flow of gas through the flow meter. The flow meter is calibrated at several different rates of flow, and a smooth curve is drawn showing the rate of flow as a function of the difference in liquid levels (Fig. 59). A convenient form is now available which is made entirely of pyrex glass. A graduated tube is mounted vertically in a larger tube, and the height of the mercury or other liquid and the displacement due to the passage of gas is read directly on the tube. The rate of flow is nearly a straight-line function of the scale reading, except when complicated by turbulent flow, and the rate of flow corre-

sponding to any reading of the scale may be interpolated with accuracy. The factors involved in the theory and use of the flow meter have been discussed by Benton.[1]

The air or other gas is passed through the flow meter by a displacement method, and a stopcock is turned so that the water or other liquid used in the manometer is maintained continuously at a constant setting.   The time taken for a unit volume to pass through is determined accurately with a stop watch.   Capillary tubes of different bores may be used for different velocity ranges.

Another type of flow meter, sometimes called a rotameter, is finding use in the measurement of the flow of both gases and liquids.   A vertical tube provided with a linear scale has a larger internal diameter at the top than at the bottom.   When gas rushes upward through this tube it carries a small float upward.   The greater the flow of gas the higher the float rises, but at the greater flows the leakage around the sides is larger, and the net result is that the rate of flow is a linear function of the height of the float.   In another form the internal bore of the tube is uniform, and a long float with tapering sides is used.

Manometers

The closed-end manometer shown on page 4 is readily made from a U tube and a wooden meter stick.   A steel or brass scale is necessary when an accuracy greater than 0.2 mm is required.   The glass tube, preferably of pyrex, should not be less than 1 cm in diameter.   It is essential to use pure mercury (page 444) and to boil out all occluded air. The tube is inverted and connected to a vacuum pump or water aspirator and heated gently and cautiously with a moving flame, throughout the length of the mercury.   If any air remains trapped between the mercury and the wall, it will come out later and give a low reading.

The height of mercury, corresponding to a definite pressure, changes with the density of the mercury, and it is necessary to refer the barometer readings to 0°C. as a standard temperature.   At room temperature, the barometer usually reads 2 or 3 mm too high.   A table of corrections is given on page 451. which applies to a barometer having a glass tube and a brass scale.

A mirror on the scale helps to avoid parallax, the eye and its image forming a straight line across the top of the meniscus, which is perpendicular to the scale.   More accurate readings can be taken with a cathetometer (page 415).   Short manometers recording pressures of 10 cm and less are used in vacuum distillations.

[1] BENTON, *Ind. Eng. Chem.*, **11**, 623 (1919).

Open-end manometers are easier to make than the closed-end manometer just described, because they do not have to be boiled out. They give the difference in pressure between the vessel and the atmosphere, and the absolute value of the pressure is obtained by subtracting this reading from (or adding it to) the barometer reading. They require one more reading than the closed-end or vacuum manometers. The closed-end manometers are superior in this respect, for they are quite independent of barometric fluctuations.

Mercury is usually used as the liquid, but any nonvolatile liquid may be used if it is not too viscous and if its density is known. The manometer readings are converted into the equivalent millimeters of mercury from a knowledge of the densities. Paraffin oil, nitrobenzene, bromonaphthalene, water, or other liquid may be used for small pressure differences. A suitable dye may be used to color the liquid so that it can be easily seen. A manometer liquid, about four times as heavy as water, can be made by dissolving mercuric iodide in a concentrated solution of potassium iodide, the exact density being determined with a pycnometer. Open-end manometers are usually preferred for liquids of this type.

McLeod Gage.—The McLeod gage, shown in Fig. 60, is used extensively for low-pressure measurements. A large volume of gas V, at the unknown pressure p, is compressed to a small volume v, and the corresponding pressure P is measured. The original low pressure p is then easily calculated with Boyle's equation $p = Pv/V$, which holds quite accurately for gases at low pressures. Almost any pressure, from millimeters down to millionths of a millimeter, can be measured, depending on the ratio of v to V.

FIG. 60.—McLeod gage.

A large bulb A, not over 500 ml in volume, terminates in a small capillary (not less than 0.5 mm in diameter), which is closed with a flat seal. A tube at least 760 mm long filled with mercury extends below the bulb, and attached to it is a stout rubber tube with mercury reservoir C. When the reservoir is lifted to a higher level, the mercury rises, traps the air in A by cutting it off at D, and continues to rise, forcing the air into the capillary B. The mercury rises to a higher level in the capillary E, which is of the same diameter as B. Both capillaries are taken from the same piece of glass to avoid unequal capillary effects.
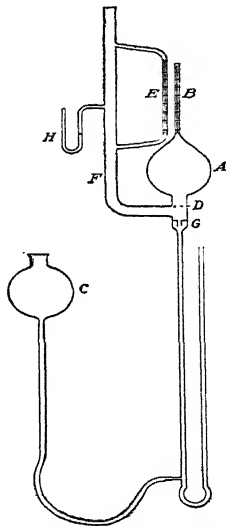
The mercury rises higher in E than in B because the latter contains gas under pressure; the difference in level h is a measure of the pressure p of the gas in B. The volume v, at different levels in the capillary B, is determined accurately by filling with mercury and weighing, and the volume V of the bulb is determined in like manner. The reservoir is set in a clamp at such a height that the mercury rises to a point in E which is just opposite the top of the closed capillary B. If v_0 is the volume of capillary B per millimeter and h is the length of the column filled with gas, then hv_0 is the total volume of gas v in the closed capillary at the pressure P or h.

Substituting into the equation $p = Pv/V$,

$$p = \frac{h^2 v_0}{V}$$

The various levels h, corresponding to pressures of 10^{-6}, 10^{-3} mm, and intermediate pressures, are marked on a scale. The divisions are smaller at the lower pressures.

The connecting tube F leading to the evacuated apparatus has a large diameter to permit rapid attainment of equality of pressure in all parts of the system. The trap G is designed to catch any air bubbles arising from the mercury column. The little U tube H indicates when the pressure is down to a few millimeters.

The mercury is purified (page 444), the rubber tube is boiled with sodium hydroxide to remove sulfur, and the glass is cleaned with chromic acid, rinsed, and evacuated while heated. Better results are obtained after the gage has been in use for a while.

Many modifications of the McLeod gage are in use. In one form a mercury reservoir is attached just below the bulb and suction is applied to the reservoir to pull the mercury down. In this type, the long tube of mercury is unnecessary, and the mercury can be kept cleaner because the rubber tube is eliminated.

Quartz–fiber Gage.—A long quartz fiber set in vibration is damped by collision with surrounding gas molecules, and it is possible to calculate the pressure of the gas by observing with a telescope and micrometer eyepiece the amplitude of the vibration at successive time intervals. This gage was used by Haber and Kerschbaum[1] and by others. Harmonic vibrations are eliminated in the bifilar quartz-fiber manometer of Coolidge[2] which is capable of measuring pressures up to 0.1 or 1 mm, with accuracy. The gage is calibrated with a perma-

[1] HABER and KERSCHBAUM, *Z. Elektrochem.*, **20**, 296 (1914).

[2] COOLIDGE, *J. Am. Chem. Soc.*, **45**, 1637 (1923).

nent gas and a McLeod gage. The observations permit a calculation of PM, where P is the pressure and M the molecular weight.

This type of micromanometer is especially valuable in chemical investigations where the gas may be affected by the mercury of a McLeod gage or decomposed by an ionization or hot-wire gage. It is suitable also for work at high temperatures and has found several applications.[1]

Thermal-conductance Gage.—The pressure of a gas at low pressures may be determined by the rate at which heat is conducted away from a heated wire. In the Pirani[2,3] gage, the resistance of an electrically heated wire is measured with a Wheatstone bridge, while the heating current is maintained at a constant value. The gage is calibrated with a McLeod gage, and the curve is nearly linear from 0.01 to 0.08 mm of mercury. A tungsten filament in a modified electric-light bulb can be used as the heating wire. A wire temperature of about 100°C. is satisfactory. This Pirani gage is used in industrial work.

Other Micromanometers.—There are many other types of micromanometers. The Knudsen gage[4] depends on the bombardment of a gold leaf by molecules under a temperature gradient. Radiometer devices and torsion devices are suitable for low pressures, and depend for the effect directly on the pressure. Tilting manometers, designed originally by Rayleigh, with mercury and a float actuating a long optical lever, are satisfactory down to hundredths of a millimeter. Ionization gages are extensively used for low-pressure measurements. The amount of current carried is a function of the pressure.[5,6]

All-glass Manometers.—For pressure measurements of corrosive gases or gases at high temperatures, a manometer made entirely of glass is desirable. Several different types are available, as summarized in Fig. 61, all of which depend on balancing a measured air pressure against the unknown pressure through a thin glass diaphragm. The zero point of the diaphragm is determined by the reflection of a beam of light, the motion of a pointer, the motion of an enclosed liquid, a clicking sound, or the closing of an electric circuit.[7] The latter type is shown on page 134. The diaphragm is suitable for pressures above

[1] HICKMAN, HECKER, and EMBREE, *Ind. Eng. Chem. Anal. Ed.*, **9**, 264 (1937).

[2] HALE, *Trans. Am. Electrochem. Soc.*, **20**, 243 (1911).

[3] DuMOND and PICKELS, *Rev. Sci. Inst.*, **6**, 362 (1936).

[4] KNUDSEN, *Ann. Physik*, **44**, 525 (1914).

[5] DUSHMAN and FOUND, *Phys. Rev.*, **17**, 7 (1921); **23**, 734 (1924).

[6] TAYCOX and WEINHART, *Rev. Sci. Inst.*, **2**, 401 (1931).

[7] DANIELS, *J. Am. Chem. Soc.*, **50**, 1115 (1928).

10 mm, and it is usually accurate to about 0.2 mm.   Pyrex may be used up to about 400°C., but above this temperature quartz is necessary.   In making quartz diaphragms, the end of a platinum wire is melted and frozen into a thin quartz capillary which is then sealed into position.

Manostats.—Barometer fluctuations are troublesome in some work, particularly in the distillation of pure liquids, where 0.3 to 0.4 mm difference in pressure may change the boiling point by 0.01°.   The
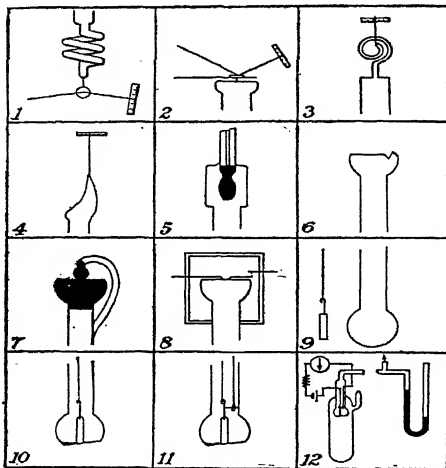
Fig. 61.—Devices for measuring gas pressures in all-glass vessels.

manostat shown in Fig. 62 maintains a constant pressure to within 0.02 mm.[1]   A barometer, connected to a large reservoir bottle, is provided with a platinum wire which can be set to give an electrical contact at 760 mm, or any other specified pressure.   The reservoir bottle is connected with the distilling flask or other apparatus, and when the pressure falls slightly below 760 mm, the electrical circuit is completed and the relay is closed.   The relay then operates an electromagnet, which attracts an iron lever arm attached to an easily turning metal stopcock.   A little compressed air is thus admitted, and the mercury column is forced back, breaking the relay circuit and stopping the supply of air.   A very small leak is provided so that the relay and stopcock operate several times a minute.

[1] MATHEWS and FAVILLE, *J. Phys. Chem.*, **22, 3** (1918).

The Bureau of Mines has developed a manostat for use in vacuum distillations. It is attached to a vacuum oil pump, and maintains any pressure between 1 and 100 mm within 0.5 mm.[1]

A simple and effective automatic pressure regulator has been described by Coffin,[2] in which the pressure is controlled by the thermal expansion of gas surrounding an electric heating coil in a closed bulb. When the mercury falls below a predetermined level, the electrical
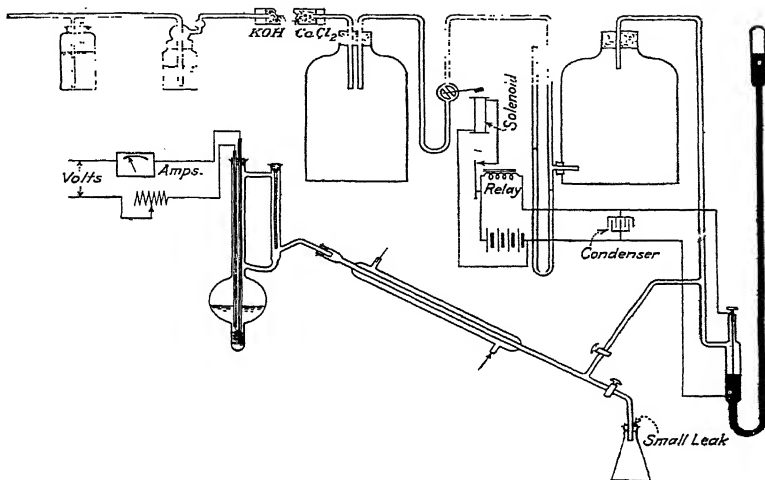
Fig. 62.—Manostat and distillation apparatus.

circuit is broken and a relay is released. The electric heating coil is thus automatically started, and the gas expands until the mercury level is again reached and the relay closed.

Several other manostats have been described.[3]

Vacuum Pumps

Water Aspirator.—The water aspirator is the cheapest and most common apparatus used for evacuation. It is limited by the vapor pressure of the water. A jet of water is forced through a small orifice

[1] DEAN, HILL, SMITH, and JACOBS, *Bur. Mines Bull.* 207, 82 (1922).

[2] COFFIN, *J. Am. Chem. Soc.*, **55**, 3646 (1933).

[3] HUNTRESS and HIRSCHBERG, *Ind. Eng. Chem. Anal. Ed.*, **5**, 144 (1933); JACOBS, *Ind. Eng. Chem. Anal. Ed.*, **7**, 70 (1935); EMERSON and WOODWARD, *Ind. Eng. Chem. Anal. Ed.*, **9**, 347 (1937).

into a narrow chamber with sloping sides in such a way as to draw in air from a side tube. Good aspirators of this type are simple and inexpensive. They can evacuate a liter flask down to about 20 mm in a minute.[1]

Oil Pump.—Motor-driven oil pumps are very convenient and efficient, quickly giving a vacuum of 0.001 mm. An eccentric cylinder rotates in a bath of oil, in such a way as to trap air on one side of the chamber and force it out on the other as it completes its revolution.
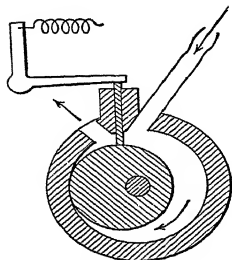
Fig. 63.—Principle of the oil vacuum pump.

A cross section of one of the units of the "Hyvac" pump is shown in Fig. 63. A scraper is forced down by a spring on the cylinder as it rotates around its axle (which is off center), and this scraper deflects into the exit tube all the gas which has been swept out by the revolution. In this way, a vacuum is created in the inlet tube.

There are two units of this type in series, both operating on the same axle in a metal box filled with oil. The exit gas passes into a settling box before coming out of the pump, in order to prevent loss of oil by foaming. A ball-and-socket valve in the outlet tube stops the backward flow of oil when the pump is stopped. A high-grade oil is necessary, having a low vapor pressure and just the proper viscosity.

Vapor Pumps.—Whereas water aspirators are useful down to 20 mm and oil pumps down to 0.001 mm, vapor pumps can evacuate down to a millionth of a millimeter. They depend on the same general principle of effusion as the water aspirator. An oil pump is usually necessary as a backing pump to make possible the proper operation of the mercury-vapor pump. A typical mercury-vapor pump is illustrated in Fig. 64. Mercury is vaporized with an electric heating coil (or a gas flame) and shot out of a jet into a long tube. The vapor condensed in the tube is returned to the reservoir. Usually the tube is cooled with a water jacket. If air cooling is used, asbestos cord is wound around the pump to shield it from air currents which would cause unequal condensation and unsatisfactory evacuation. Mercury has a low vapor pressure, but it is nevertheless sufficient to cause diffusion of mercury into the system being evacuated. For this reason a tube in liquid air is interposed as a trap, as shown at the right in Fig. 64. The vacuum-walled bottle is kept filled with liquid air, and the mercury vapor and other vapors are prevented from further diffusion. The pumps are usually made of pyrex glass, which has a

[1] HARRINGTON, *J. Optical Soc. Am.*, **14**, 1 (1927).

low temperature coefficient. Many different types of air-cooled and water-cooled mercury-vapor pumps are available.

Certain high-boiling organic liquids may be used in place of mercury in vapor pumps.[1] The liquid, n-butyl phthalate may be used with a trap cooled with solid carbon dioxide. A special petroleum oil
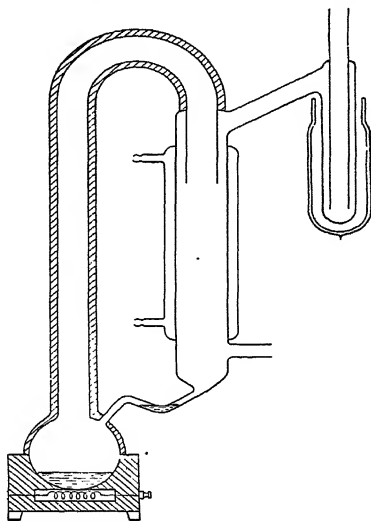
Fig. 64.—Mercury vapor pump.

"Apiezon B" is still better and can be used to give a pressure less than 10^{-5} mm, with a trap cooled only with cold water. Special oils have been developed for obtaining very high vacuum, so that it is now possible to obtain better than 10^{-6} mm without using cold traps. Ocyoil (2-ethyl hexyl phthalate) and octoil-S (2-ethyl hexyl sebacate) are commercially available. Pumping speeds of 15 liters per second measured at 10^{-4} mm can be obtained.

A large vapor pump, of steel tubing 20 cm in diameter, is described by Harrison.[2]

Other Methods.—The Gaede molecular pump[3] depends on the principle that a rapidly moving surface at low pressures will carry some gas along with it. A metal cylinder is rotated at a high velocity in a

[1] HICKMAN and SANFORD, *Rev. Sci. Inst.*, **1**, 140 (1930).

[2] HARRISON, *Rev. Sci. Inst.*, **4**, 652 (1933).

[3] GAEDE, *Ann. Physik*, **41**, 337 (1913).

casing only slightly larger.   Gas from an inlet is whirled around nearly the whole circumference of the casing and then discharged.   The surface area is increased by placing a number of projecting rings on the casing, which nearly engage corresponding grooves in the drum.   It is possible with this pump to decrease the pressure to one hundred thousandth of that of the former pump.   When combined with a
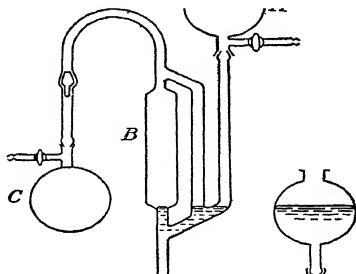
G. 65.—Toepler pump.

mercury-vapor pump, the Gaede pump can produce a vacuum of nearly 10^{-9} mm.

The Toepler pump operates by alternately raising and lowering a mercury reservoir, as shown in Fig. 65.   It is slow and awkward, but useful in transferring samples of gas (particularly at low pressures) from one vessel to another.

Each time the mercury level is lowered, the gas from A expands into B, and each time it is raised, the gas is forced from B into C, or into the room.   The height of the mercury tube must be greater than the barometer height.

A very high vacuum can be obtained quickly and easily by attaching to the apparatus a tube of recently heated, activated charcoal and immersing the tube in liquid air.

Charcoal and liquid air form a dangerous mixture which explodes with great violence. If a glass tube containing charcoal is immersed in liquid air, it should be surrounded with a thin metal tube (preferably of Monel metal to mimimize heat conductance and loss of liquid air). The tube should extend only 2 or 3 cm above the liquid air. This precaution applies also to organic vapors condensed out in a liquid air trap.

Vacuum Technique.—At low pressures, the mean free path of the molecules is large, and connecting tubes must be of large diameter. When working at pressures approaching a millionth of a millimeter, the diameters should be at least 3 cm.

The surface of metals and glass contains adsorbed gases which continue to be evolved slowly in an evacuated space. It is often necessary to bake out glass vessels at a temperature just below the softening temperature during the evacuation. The surfaces should be cleaned first with hot sulfuric acid and potassium dichromate and thoroughly rinsed and baked. Metals should be thoroughly cleaned with acetone or other solvent and heated while the apparatus is being pumped out.

Stopcocks cannot be used in high-vacuum work, but mercury traps are sometimes useful. The mercury level is raised so as to flow up from the bottom of a U tube and fill both sides of the tube, thus shutting off connection between two vessels. A liquid-air trap is necessary to prevent diffusion of mercury vapor. Loosely ground valves, containing sealed-in iron cores, may be set and lifted with magnets when an absolutely tight joint is not needed. When low pressures exist on both sides of the valve, they are often adequate.

Leaks are very troublesome in high-vacuum work, and the smaller leaks are often difficult to find. A small high-frequency Tesla coil (sold by apparatus manufacturers) forms a very convenient "leak chaser," which produces a concentrated spark in the walls of an evacuated vessel wherever a tiny hole exists. In certain types of investigation on gases at reduced pressure, this testing for leaks in new glass apparatus should become a matter of routine.

The subject of high-vacuum technique and apparatus is completely covered by Strong.[1]

[1] STRONG, "Experimental Physics," Chap. III, Prentice-Hall, Inc., New York (1940).

CHAPTER XVII

PHYSICAL PROPERTIES OF LIQUIDS

Distillation

Boiling Point.—The boiling point of a liquid is a characteristic property which is useful for purposes of identification and for the determination of purity. The boiling point of a pure liquid is rather easily determined in an ordinary distilling flask, but certain precautions should be observed. The thermometer should be short so that the whole column of mercury is surrounded by the vapor, or else a rather unsatisfactory stem correction is necessary (page 421). The thermometer bulb should be near the outlet tube so that it registers the temperature of the exit vapors. The boiling should not be so violent as to cause spray to reach the thermometer bulb or so rapid as to build up a pressure in the flask appreciably greater than atmospheric pressure. To avoid splashing, the flask should not be over half full.

One of the greatest sources of error comes from overheating the neck of the flask and heating the thermometer bulb by radiation. A large gas flame is particularly bad in this respect. A small gas flame without wire gauze or sand bath is better. It is a good plan to heat the distilling flask in a beaker of hot water (or oil at higher temperatures) to a temperature only slightly above the boiling point of the liquid as determined with an ordinary thermometer in the water bath. A thin-walled cylindrical tube placed between the thermometer and the flask in the vapor is sometimes used, to minimize radiation.

Overheating may be minimized by using a small electric heating spiral, coiled in an asbestos box. Three meters of No. 26 nichrome wire provides a satisfactory heating unit at 110 volts for low-boiling liquids. In this way the heat is localized at the bottom of the flask and does not spread to the upper part of the flask. Heating coils for 110 volts are available for replacements in electrical household appliances.

An electric heating coil immersed in the boiling liquid offers a good means of supplying the heat, for there is no overheating of the thermometer, and superheating and bumping of the liquid are also eliminated. The Richards–Mathews distillation flask, shown in Fig. 62, has been found very satisfactory for distillations at either reduced or

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normal pressures.   The vapor rises from the electrically heated liquid and passes over into the side tube, completely enveloping the thermometer, which is suspended on a platinum wire attached to a glass hook on the stopper.   The trap at the bottom allows condensed liquid to return to the boiling flask.   This apparatus gives good distillation and ensures a proper thermometer reading, since the thermometer is completely within the vapor.   Both stoppers may be made of glass if corks or rubber stoppers need be avoided.

This design gives good circulation of the liquid and allows the heating to be carried on until only a small volume of liquid remains.   The heating coil of bare platinum wire is sealed through long glass tubes which pass down through the stopper of the flask.   Electrical connection is made by welding copper wires before sealing in.

Superheating.—The liquid should boil smoothly and steadily, but in some cases there is a tendency for the liquid to become heated above its boiling point.   Superheating is due to the fact that the vapor pressure of a liquid is abnormally low at a concave surface.   It may be prevented by introducing, in the body of the liquid, comparatively flat surfaces between the vapor and liquid phases.   Any means of trapping small air bubbles in the liquid is effective.   Small chips of unglazed porcelain with air enclosed in the pores or pieces of platinum or platinized platinum are effective in the prevention of bumping.   The smoothest boiling is obtained with the internal electric heating coil described above.

Distilling flasks covered with sintered glass powder are effective in preventing bumping.[1]   Some of the same glass of which the flask is made is ground in a mortar and moved around inside while the flask is heated in a blast lamp to its softening temperature.   Again, the surface may be coated with silica by evaporating a dilute solution of sodium silicate, heating to dull-red heat, cooling, and treating with dilute hydrochloric acid and rinsing.[2]

Bumping is particularly apt to be troublesome under reduced pressure, and it may be advisable to have a small stream of air bubbling through the liquid.   A tube is inserted in the stopper, with its lower end drawn out into a capillary extending into the liquid.   Its upper end is closed by a rubber tube and adjustable pinchcock to control the rate of bubbling.

Micro Boiling-point Apparatus.—In the Smith and Menzies[3] method, shown in Fig. 66, only a small quantity of liquid is necessary.

[1] MORTON, *Ind. Eng. Chem. Anal. Ed.*, **6**, 384 (1934).

[2] SWIETOSLAWSKI, *J. Chem. Ed.*, **5**, 469 (1928).

[3] SMITH and MENZIES, *J. Am. Chem. Soc.*, **32**, 897 (1910).

It is placed in the inverted bulb as shown, and this is strapped to the bulb of a thermometer in a bath of water or other transparent liquid.

The liquid of the bath should be immiscible with the liquid under investigation. The temperature is raised gradually, and when the boiling point is reached a stream of bubbles issues from the bulb. A slight cooling below the boiling point causes immediate cessation of the bubbling. The temperature of bubbling is determined several times and averaged. A correction is applied to the barometer reading to allow for the hydrostatic pressure of the bath from the outlet of the little tube to the surface.
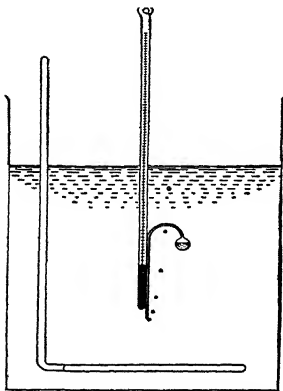
6.—Micro boiling point apparatus.
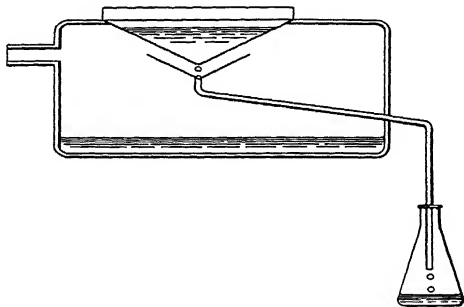
Fig. 67.—Apparatus for distillation at very low pressures.

High Vacuum Distillation.—Special techniques for distillation of material of low volatility have been developed by Hickman[1] and others. Theoretically, it is possible to distill and condense without decomposition high-boiling oils and even materials like sucrose. The gas pressure surrounding the liquid (or solid material) is merely kept below the vapor pressure with an efficient vapor pump. However, with ordinary flasks and condensers a simple calculation based on the kinetic theory of gases will show that the time required is so very long that the distillation is utterly impractical. It is necessary to use wide vessels with extremely short distances between the vaporizing material and the colder condenser. In order to meet these requirements, vessels of the type shown in Fig. 67 have been devised. The one shown is the Hick-

[1] HICKMAN, *J. Franklin Inst.*, **213**, 119 (1932); HICKMAN and WEYERTS, *J. Am. Chem. Soc,* **52**, 4714 (1930).

man molecular still which can be purchased from supply houses. A similar one can be constructed from two Erlenmeyer flasks, cracking the outer one in two, to admit the smaller one, and sealing the two halves together again.

The tops of two vacuum desiccators may be set together so that a large flat condensing surface is placed directly over a flat dish containing the liquid or solid to be evaporated.[1] A water-cooled Erlenmeyer flask is supported from the upper hole, and a support for the dish, an electric heating circuit, and a thermocouple circuit pass through the bottom hole.

Distillation with short paths at very high vacuum is now important in certain industrial operations such as the separation of sterols from fish oil.[2] The measurement of the temperature of the vapor is not practical in short-path distillation, but information can be gained by distilling a number of known substances at different temperatures and plotting a curve of material condensed against temperature. In this way the relative temperatures at which an unknown material comes over can be determined by reference to some known material.[3] These separations may be made very conveniently with a series of pilot dyes[4] of different volatilities which condense to give a colored deposit.

Vapor Pressure

Static Method.—In the simplest method the liquid is contained in a bulb connected with a mercury manometer and a vacuum pump. The greatest source of error lies in the presence of air or other permanent gases which have been dissolved by the liquid or trapped by the mercury. Enough liquid is evaporated with the pump to sweep out all the gases. The evacuation is repeated until further evacuation gives no lowering of the vapor pressure. The whole apparatus should be thermostated. The method has been used by many investigators.

The Ramsay and Young[5] method without thermostating is described on page 23.

The isotenoscope of Menzies[6] is a simple device for determining the vapor pressure of a liquid, or a solution, and indicating when the dissolved air has been removed. It is shown in Fig. 68. The bulb is

[1] CAROTHERS and HILL, *J. Am. Chem. Soc.*, **54**, 1557, 1561 (1932).

[2] HICKMAN, *Ind. Eng. Chem.*, **32**, 1451 (1940).

[3] EMBREE, *Ind. Eng. Chem.*, **29**, 975 (1937).

[4] HICKMAN, *Ind. Eng. Chem.*, **29**, 968, 1107 (1937).

[5] RAMSAY and YOUNG, *Phil. Trans.*, **175**, 461 (1884).

[6] SMITH and MENZIES, *J. Am. Chem. Soc.*, **32**, 1413 (1910).

half-filled with liquid, some liquid is placed in the bottom of the U, and the whole tube is mounted in a water bath or oil bath which is stirred while the liquid is brought to any desired temperature. The tube is connected to a manometer and vacuum pump as shown in Fig. 5, page 21. If any dissolved air remains in the liquid, the liquid in the U tube will be displaced and the liquid must be further degassed by boiling. Only when the liquid columns in the little U tube are level does the manometer give the correct vapor pressure.

The vapor pressures of liquids may be measured at pressures somewhat above atmospheric.[1]
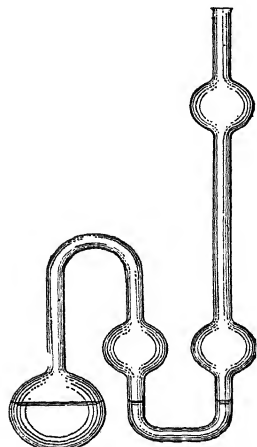
FIG. 68.—Menzies isotenoscope for vapor pressures.

Air-saturation Method.—In this method, a measured volume of air, or other inert gas, is saturated by passing it through the liquid at a definite temperature. The quantity of liquid vaporized is obtained from the loss in weight of the liquid, or by removal of the vapor from the gas stream in weighed absorbing tubes. From the weight of the vapor and the volume of the gas, the partial pressure of the vapor, P, is calculated by the formula

$$P = \frac{g}{MV} RT$$

where R is the gas constant, T is the absolute temperature, and V is the total volume of gas (including air and vapor) which contains g grams of vapor of molecular weight M. When V is expressed in liters and P in atmospheres, R is expressed in l. atm. deg.$^{-1}$ mole^{-1}. In case the vapor pressure is very low, it can be neglected in comparison with the atmospheric pressure in calculating the volume of the gas.

Premature condensation must be avoided if the vapor is to be absorbed and weighed, and at higher temperatures the saturator, absorption tubes, and connecting tubes are all immersed in the thermostat. It is essential to saturate completely the air or other gas with the vapor of the liquid; but, on the other hand, there must be no stoppage of the apparatus which might build up a changing or an unknown hydrostatic pressure. If the air is passed through the saturator so slowly that a still slower rate gives no greater vapor pressure, it may be concluded that the air is completely saturated.

[1] FRANCIS and ROBBINS, *J. Am. Chem. Soc.*, **55**, 4339 (1933).

The air-saturation method has been used in precision researches by Washburn[1] for the determination of vapor pressures of aqueous solutions, and by Baxter[2] for the vapor pressure of iodine. It has been used for vapor pressures of metals and salts at high temperatures, and it is suitable for solids as well as for liquids.

Density

Hydrometer.—The specific gravity of a liquid may be most easily determined with an ordinary hydrometer. Hydrometers may be purchased in sets that cover a wide range of densities, each hydrometer retaining a high sensitivity over a limited range. They find extensive use in industrial operations and in making up solutions of definite concentration, and particularly in testing storage batteries.

Westphal Balance.—The Westphal balance is more accurate than the hydrometer. It depends on the principle of Archimedes, according to which the buoyant effect is directly proportional to the weight of the liquid displaced. The sinker is suspended in pure water, with the unit weight in position, and a threaded counterpoise is turned until the pointers are opposite each other. The sinker is then dried and suspended in the new liquid. The smaller weights are set at the proper places on the scale so as to restore the point of balance. There are the three riders corresponding to 0.1, 0.01, and 0.001, and the scale is divided into 10 equal parts. The position on the scale gives the numerical value for each rider; *e.g.*, if the 0.1 rider is at 9, the 0.01 at 8, and the 0.001 at 7, the specific gravity is 0.987.

The temperature is read directly on a thermometer, which is enclosed in the sinker. A very fine platinum wire is used for suspending the sinker; the surface-tension effect on this wire is negligible for ordinary work, but for accurate work it may prove to be a source of error. The wire should be immersed to the same depth for each measurement.

The same principle of weighing a sinker while suspended in a liquid is used in the chainomatic balance, shown in Fig. 69. With this more elaborate instrument, densities may be determined quickly with an accuracy of 1 part in 10,000. The value of the instrument is increased by the introduction of an electric heating coil and switch, to maintain the liquid at a definite temperature.

Pycnometers.—Pycnometers are vessels with capillary necks, in which a definite volume of liquid is weighed. The volume is determined by weighing the vessel filled with water at a definite temperature.

[1] WASHBURN and HEUSE, *J. Am. Chem. Soc.*, **37**, 309 (1915).
[2] BAXTER, HICKEY, and HOLMES, *J. Am. Chem. Soc.*, **29**, 127 (1907).

The Ostwald-Sprengel pycnometer, shown on page 96, is a standard type, in which the liquid is drawn in as in a pipette. The liquid is adjusted to a definite mark on the capillary. The greatest error is usually due to the adsorption of an uncertain amount of moisture by the glass, and it is necessary to wipe the pycnometer with a damp cloth and allow it to stand in the balance case for several minutes before weighing. A similar pycnometer of approximately the same volume may be used to advantage as a counterpoise. The
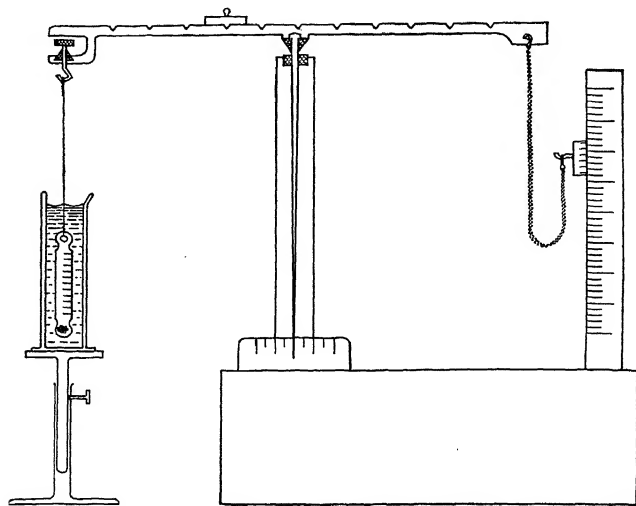
FIG. 69.—Chainomatic balance for determining the density of liquids.

size of the pycnometer depends on the quantity of liquid available and the precision demanded; 10- and 25-ml sizes are often used. Pycnometers of fused quartz are best, but pyrex or soft glass is satisfactory.

The pycnometer shown in Fig. 70 is recommended as accurate and convenient. The neck is short and ends in a very small hole which is barely visible (0.01 mm in diameter). In this way, evaporation is nearly eliminated, and the pycnometer is given a definite volume, which requires no adjustment. It can be made readily by drawing down a larger tube to a thick-walled neck and cutting off or filing down to a smooth end. Knobs of glass are attached at the sides of the neck

to assist in suspending the pycnometer in the balance case with platinum or nickel wire.

The pycnometer is cleaned, rinsed, and filled by placing in a tube which can be evacuated with an efficient water aspirator (or vacuum pump). The liquid is placed in the tube, the pycnometer is introduced, neck up, and forced below the level of the liquid with a glass tube laid on top. The stopper is inserted and the whole system is evacuated, until the liquid boils for a short time and the air in the pycnometer is forced out through the liquid. The connection to the aspirator is closed and the stopcock is then opened to admit air at atmospheric pressure, thus forcing the liquid into the pycnometer. Usually it is not completely filled, and the process is repeated. A second or a third evacuation followed by an inrush of air usually completes the filling. A plug of cotton or glass wool in the tube prevents solid particles from entering when the vacuum is released. For small pycnometers, the neck of a broken glass-stoppered volumetric flask may be used for making the filling tube. A test tube and two-hole rubber stopper with two stopcocks may be substituted for the glass-stoppered filling tube provided that the stopper has been boiled in sodium hydroxide solution to remove sulfur. Care must be exercised to prevent small particles from falling into the liquid.

Fig. 70.—Pycnometer and filling device.

This pycnometer is not suitable for filling at temperatures below room temperature.

For determining the density of a solid, a pycnometer with a wide mouth is necessary in order to admit the solid. The ordinary type is a small bottle with a ground-glass stopper through which is bored a fine capillary.

The bottle is filled with water, and the stopper is inserted firmly, after which it is placed in a thermostat. The excess liquid is wiped off, and the pycnometer is dried and weighed. The pycnometer is weighed empty and again with the solid. After filling with water (plus the solid), it is weighed again, and all the data are then available for calculating the weight and volume of the solid, and its density. In case the solid is soluble in water, some other inert liquid is used, and its density is determined.

The greatest source of error in determining the density of a solid ies in the adsorption of air by the solid. For this reason the pycnome-

ter containing the solid and some liquid is set into a larger bottle, connected to a vacuum pump, and evacuated until all air bubbles have ceased rising from the solid; then the pycnometer is filled completely.

The ground-glass stopper is a source of error, for the stopper may not be forced down to exactly the same depth every time.   This difficulty has been overcome in the pycnometer of Johnston and Adams,[1] in which a fairly wide mouth with a thickened end is ground and polished absolutely flat, and closed with a flat piece of glass.   The contact between these two pieces of optically flat glass is so good that when the top is pressed down the excess liquid is forced out, and the joint is just as tight as a ground-glass stopper joint.   There is no evaporation, and there can be no uncertainty about the depth of the stopper or the volume of the flask.

Floating Equilibrium.—The objection to the wire projecting through the surface of the liquid in the case of the Westphal balance can be eliminated by having a bulb so carefully adjusted that it neither sinks nor rises in the liquid.

Lamb and Lee[2] obtained accurate results by placing a piece of iron in the float and measuring the strength of the electromagnetic field that was just necessary to keep the bulb in a position of equilibrium without sinking or rising.

This method has been extended by Hall and Jones[3] and by Hall and Alexander[4] to obtain density measurements on water to 1 part in 10 · million for studies of the exchange of heavy oxygen.   A precision up to 1 part in 50 million was achieved.   A quartz swimmer was kept from rising or falling by two opposing solenoids each operating on a different battery.   An interesting feature of this investigation is the fact that by working at a little above 4° the influence of temperature on the density is far less than at 25°, and close temperature control of the thermostat is much less critical.   A figure is given showing the large difference in the influence of temperature at the two temperatures.

Richards and Shipley[5] adjusted the temperature until the sinker reached a point of equilibrium, and thus obtained high precision.

Lewis and MacDonald[6] used this method for measuring the density of water containing isotopes.

[1] Johnston and Adams, *J. Am. Chem. Soc.*, **34**, 566 (1912).

[2] Lamb and Lee, *J. Am. Chem. Soc.*, **35**, 1666 (1913).

[3] Hall and Jones, *J. Am. Chem. Soc.*, **58**, 1915 (1936).

[4] Hall and Alexander, *J. Am. Chem. Soc.*, **62**, 3455 (1940).

[5] Richards and Shipley, *J. Am. Chem. Soc.*, **36**, 1 (1914); Richards and Harris, *J. Am. Chem. Soc.*, **38**, 1000 (1916).

[6] Lewis and MacDonald, *J. Chem. Phys.*, **1**, 341 (1933).

Gilfillan[1] adjusted the hydrostatic pressure on the liquid with a mercury column until equilibrium of the bulb was obtained. He calibrated the apparatus with dilute potassium chloride solutions of known densities.

The density of solids can be determined in a somewhat similar way by mixing two liquids of different density until the solid neither rises nor sinks. The system must be evacuated to remove air from the solid. A heavy liquid like methylene iodide is mixed with a light liquid like benzene, and the density of the final mixture is determined with a pycnometer. The density of the liquid is the same as the density of the solid with which it is in floating equilibrium.

This method has been used by Hutchinson and Johnston[2] for the accurate determination of the density of lithium fluoride. The necessary precautions have been described, and the determinations were sufficiently accurate to follow the concentration of lithium isotopes[3] by electrolysis.

A mixture of bromoform, n-hexanol, and n-pentanol was used, and by adjusting the proportions a liquid of suitable density was found, which was then adjusted in temperature until the crystals neither sank nor rose when viewed through a microscope. The crystals were formed by heating to 100° above the melting point in a platinum crucible and solidifying very slowly by touching an air-cooled platinum tube.[4]

Viscometry

The Ostwald viscometer described on page 36 has been improved by Bingham.[5] The liquid is forced through a capillary with compressed air maintained at constant temperature. There are marks at the top and bottom of the bulb, and the time required for liquid to flow first up and then down is recorded.

The determination of absolute viscosities is rather difficult. It requires careful measurements of the apparatus, including the length and radius of the capillary, and some rather uncertain corrections. In one investigation a capillary tube, carefully measured, was ground into the tube.[6] Further details for the absolute measurements are given by Thorpe and Rodger[7] and by Bingham, Schlesinger, and Coleman.[8]

[1] GILFILLAN, *J. Am. Chem. Soc.*, **56**, 406 (1934).

[2] HUTCHISON and JOHNSTON, *J. Am. Chem. Soc.*, **62**, 3165 (1940).

[3] JOHNSTON and HUTCHISON, *J. Chem. Phys.*, **8**, 869 (1940).

[4] KYROPOLOUS, *Z. anorg. Chem.*, **154**, 308 (1926).

[5] BINGHAM, "Fluidity and Plasticity," p. 76, McGraw-Hill Book Company, Inc., New York (1922).

[6] BINGHAM, *J. Chem. Soc.*, **103**, 959 (1913).

[7] THORPE and RODGER, *Phil. Trans.*, **A185**, 397 (1894).

[8] BINGHAM, SCHLESINGER, and COLEMAN, *J. Am. Chem. Soc.*, **38**, 27 (1916).

Viscosities at high pressures have been studied by Hyde.[1]

The simplest method, and one that is frequently used, depends on the time taken for a sphere to fall through a given distance. It is capable of absolute measurements. The formula for the determination of relative viscosities is

$$\frac{\eta}{\eta_s} = \frac{(D - d)}{(D - d_s)} \frac{t}{t_s}$$

where η = the viscosity of the liquid.
D = the density of the sphere.
d = the density of the liquid.
t = the time.

The subscript s refers to a standard liquid, the viscosity of which is known. The sphere is discharged slowly into the tube, a few centimeters below the surface, through a glass tube slightly larger than the sphere; 1.5 mm is a suitable diameter for the sphere, and 20 cm a satisfactory height for fall. The vessel should have a diameter at least ten times that of the sphere. A steel ball, such as is used in ball bearings, makes an excellent ball for the experiment, because it is almost truly spherical. It must be free from air bubbles as it leaves the discharge tube.

This method has been studied critically by Gibson and Jacobs,[2] who find that it is capable of considerable precision. It has been used successfully for measurements of viscous liquids such as blast-furnace slags.

For opaque solutions, an audio-oscillating tube circuit may be used; when the ball passes through a coil wound on the outside of the tube, a change is produced in the sound.[3]

The MacMichael viscometer is satisfactory for viscous liquids. A horizontal disk is suspended in the liquid by means of a steel wire, and the angle of torque is measured when the outside cup is rotated at constant speed. A large range of viscosities is covered by using a series of wires of different diameters. Readings are rapid and easy. Frequent calibrations are necessary, and the corrections are not fully understood.

The Stormer viscometer with a rotating cylinder, operated by a falling weight, is widely used.

The whole subject of viscosity and viscometers is discussed adequately by Hatschek[4] and by Barr.[5]

[1] HYDE, *Proc. Roy. Soc. London*, **A97**, 240 (1920).

[2] GIBSON and JACOBS, *J. Chem. Soc.*, **117**, 473 (1920).

[3] SYMMES and LANTZ, *Ind. Eng. Chem. Anal. Ed.* 1, 35 (1929).

[4] HATSCHEK, "The Viscosity of Liquids," George Bell & Sons, London (1928).

[5] BARR, "Viscometry," Oxford University Press, London (1931).

The use of automatic timing for the transit of the meniscus of the liquid in the capillary tube, by means of a photoelectric cell, has been developed to a high degree of perfection by Jones and Talley.[1]   Details of the necessary assembly have been given by these investigators, in an article in which they also analyze sources of error in the use of viscometers.

[1] JONES and TALLEY, *Physics*, 4, 215 (1933); *J. Am. Chem. Soc.*, 55, 624 (1933).

CHAPTER XVIII

OPTICOCHEMICAL MEASUREMENTS

Apparatus of Spectrometry

The spectroscope, the spectrophotometer, and a spectrograph have been described before on pages 43, 58, and 294 for use in the visible and longer ultraviolet regions of the spectrum. For work in the ultraviolet, quartz prisms, lenses, and absorption cells are used. For the extreme ultraviolet beyond 2,000 or 1,800 Å the optical parts are made of fluorite and the spectrograph is evacuated because air is absorbing. Arcs or sparks are used as sources, but when a continuous source is needed for absorption spectra, an electrical discharge in hydrogen is recommended as given on page 394.

For work in the infrared, photographic plates specially sensitized with dyes (page 405) may be used nearly up to 10,000 Å or 1 μ. At longer wave lengths a spectrometer-thermopile assembly must be used. The thermopile responds equally to all wave lengths, but it is less sensitive than the photographic plate or the photoelectric cell. Solid filaments, stable in the air, are rendered incandescent by electricity. "Nernst glowers" or "globars" are most frequently used. The optical parts are made of various materials, depending on the range of the spectrum to be covered—glass up to 1.5 to 2.0 μ, quartz to 4 μ, rock-salt crystals (NaCl) to 15 μ, and potassium bromide crystals to 25 μ. Gratings can be used for dispersion at all wave lengths.

Large prisms and lenses of potassium bromide, sodium chloride, lithium fluoride, and other crystalline material may now be purchased, and a new field of infrared measurements is thus opened up. The crystals are made on a large scale by the Stockbarger method in which large masses of the fused salt are cooled down very slowly over many days by special electrical heating automatically controlled.[1]

The principle of the spectrometer is illustrated in Fig. 71. The prism is mounted on a plate which can be rotated by means of a drum provided with a scale of wave lengths. Quantitative measurements of emission are made by measuring the amount of energy that falls on the thermopile, using a galvanometer system. The absorption at each setting of the spectrometer is calculated by dividing the galvanometer

[1] Harshaw Chemical Co., Cleveland, Ohio.

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deflection by the galvanometer deflection obtained in the absence of the absorbing material. Measurements are laborious, for galvanometer readings must be taken at very frequent intervals throughout the region in question.

In the more elaborate investigations the galvanometer deflections are recorded automatically on a large revolving drum of photographic paper (contrast bromide paper). The drum rotates horizontally in a light-tight box, and the beam of light from the galvanometer runs out and back along a horizontal slit extending the whole length of the box.
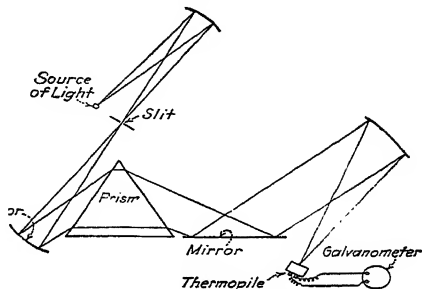
Fig. 71.—Spectrometer with thermopile.

The track of the galvanometer light is recorded on the photographic paper.

The spectrometer is adjusted for minimum deviation, and set with sodium light. The scale is calibrated, with the help of the index of refraction of the material of the prism, for sodium light and for light of standard wave lengths. The calibration is checked with the absorption bands of carbon dioxide (4.29 and 2.75 μ) in the air, and with other known absorption bands, such as the bands of chloroform or the lines of the mercury arc.

References to the technique of infrared spectrometry are given.[1]

Apparatus of Refractometry

The principles of refractometry and the construction of three typical refractometers have been described on pages 44 to 50.

[1] SCHAEFFER and MATOSSI, "Das Ultrarote Spektrum," Verlag Julius Springer, Berlin (1930); RAWLINS and TAYLOR, "Infra Red Analysis," University Press, Cambridge (1929); CROSS, Calibration of an Infrared Spectrometer with a Rock-Salt Prism, *Rev. Sci. Inst.*, **4**, 197 (1933); ROBERTSON and FOX, *Proc. Roy. Soc. London*, **A120**, 128–157 (1928); BARNES and BONNER, *J. Chem. Ed.*, **14**, 564 (1937); **15**, 25 (1938); SUTHERLAND, Infra Red and Raman Spectra, Methuen & Co., Ltd., London (1936).

The compensator (or Amici prism), which makes possible the use of white light in the Abbé and immersion refractometers, consists of two direct-vision prisms in the telescope barrel, which can be rotated in opposite directions. The direct-vision prisms are made to give dispersion, with a minimum of deviation, by cementing a dense prism of flint glass between two prisms of crown glass. If the first direct-vision prism spreads out the light into a spectrum, and if the second prism is set at the same angle, the dispersion is doubled. However, if the prism is rotated through 180°, as shown in Fig. 13, the second prism will subject the dispersed beam to an opposite dispersion, thus reproducing white light. The prism of the refractometer itself also produces dispersion, the amount depending on the refractive index of the liquid. The extent to which the prisms of the compensator must be rotated in order to offset the dispersion of the refractometer liquid and produce white light must be determined each time by trial. The reading on the compensator drum is a measure of the dispersion of the liquid.

The cup of the Pulfrich refractometer is cemented to the prism. For organic liquids, fish glue may be used. Still better is a concentrated gelatin solution containing potassium dichromate, which is exposed to bright sunlight after setting in place. Water cannot be used with these cements. For aqueous solutions, Canada balsam may be used.

The zero reading of the Pulfrich refractometer is determined as described on page 45. The Abbé refractometer is checked by placing against the upper prism a plate of glass of known refractive index supplied with the instrument. The two surfaces are held together with a drop of liquid having a higher index of refraction, *e.g.*, monobromonaphthalene. If the refractometer does not give the proper reading, it is adjusted by means of the small screw at the back of the telescope. The immersion refractometer is checked with distilled water. If the shadow edge does not fall at 15.0 for 17.5°C. or at 13.25 for 25°C., adjustment is made by means of a screw inside the micrometer drum. *Adjustments of this kind on expensive instruments should be made only by authorized persons.* The refractometers may be tested also with standard liquids of known refractive index, provided that they are absolutely pure.

The Pulfrich and the immersion refractometers may be provided with interchangeable prisms which extend the range to different refractive indices. The immersion refractometer is provided with a small metal cap with a glass bottom which fits over the prism and permits measurements to be made with small amounts of liquid.

The refractive index of liquids changes considerably with temperature, and temperature control to 0.1 or 0.2° is necessary. The refrac-

tive index of glass against air changes also, but to a considerably smaller extent. For example, in the Pulfrich refractometer, the refractive index of the prism is given for 20°, and an increase of 3° gives an increase in the refractive-index calculations of about 1 in the fifth decimal place. This temperature correction for the glass may be neglected in ordinary work at room temperature.

The refractive index varies considerably with the wave length. The compensators for use with white light are normally set for the D line *i.e.*, 5,893 Å. The Pulfrich refractometer may be used with monochromatic light of various wave lengths, usually the C, F, G, and H lines of hydrogen. These different lines (lettered originally from lines in the sun's spectrum) have the following wave lengths: C, 6,563; F, 4,861; G, 4,308; and H, 3,969 Å. The change in refractive index with wave length, known as "dispersion," is connected with the structure of organic compounds, in a manner similar to the refractive index itself.

The refractive index of a solid may be determined by holding the highly polished surface of the solid against the fixed prism of the Abbe or immersion refractometer, using monobromonaphthalene, or other liquid of high refractive index, between the two surfaces. Plastic substances may be used in the same way, coating the material directly on the face of the prism in such a way as to avoid air bubbles. When the refractometer is used for such substances, the greatest care must be taken to clean the prism after each measurement.

A few references are given below.[1]

Small differences in refractive index may be determined with great accuracy by using an interferometer. A beam of monochromatic light is split into two parts which traverse different tubes and combine again to give interference bands. An adjustable plate is included in one path and turned until the two sets of interference bands are made to match. The interferometer can be applied to the analysis either of gases or of solutions in liquids.[2]

Apparatus of Microscopy

By means of a simple convex lens, an object may be subjected to a single magnification. The compound microscope is an instrument by means of which a double magnification is obtained, for the magnified image of an object, formed by the objective of the microscope, is again magnified by the ocular, or eyepiece. The principal parts of a com-

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[1] WAGNER, "Tabellen zum Eintauchrefraktometer," Sondershausen (1907); AUERBACH, *Z. angew. Chem.*, **35**, 114 (1922); LÖWE, *Chem. Ztg.*, **45**, 25, 52 (1921).

[2] WILLIAMS, W. E., "Applications of Interferometry," Methuen & Co., Ltd., London (1930).

pound microscope, with the formation of the various images, are shown
in Fig. 72.
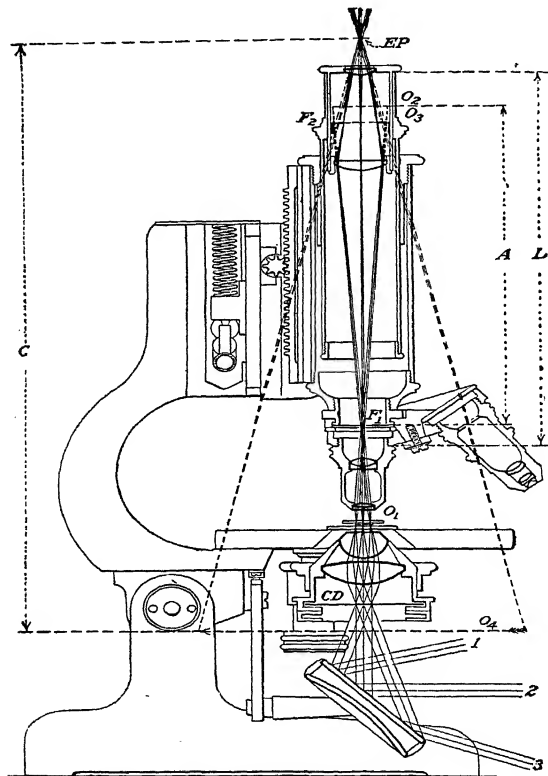
FIG. 72.—Microscope.

F_1 = Upper focal plane of objective.
F_2 = Lower focal plane of eyepiece.
A = Optical tube length = distance between F_1 and F_2.
O_1 = Object.
O_2 = Real image in F_2, transposed by the collective lens.
O_3 = Real image in eyepiece diaphragm.
O_4 = Virtual image formed at the projection distance C 250 mm from
EP = Eyepoint.
CD = Condenser diaphragm.
L = Mechanical tube length (160 mm)
1,2,3, = Three pencils of light coming from different points of a distant illuminant, for instance,
a white cloud, which illuminates three different points of the object.

The resolving power (R.P.) of a microscope is a measure of its
capacity to reproduce minute details of the structure of the object in

the image. It is directly proportional to a quantity called the numerical aperture (N.A.), and inversely proportional to the wave length λ of the light employed.

$$R.P. \quad \frac{N.A.}{\lambda}$$

This formula is valid only for central illuminating; if sufficiently oblique illumination is used, the resolving power may be almost doubled. The increase in resolving power is proportional to the sine of one-half the angle at which the light enters the objective. The resolving power also increases with an increase in the refractive index of the medium intervening between the front lens of the objective and the cover glass over the specimen. Thus, by using water-immersion and oil-immersion lenses, the resolving power can be further increased.

Eyepieces equipped with a measuring scale are known as "micrometer eyepieces." Such eyepieces are very useful in connection with the ultramicroscope (page 361). The scale may be calibrated in absolute units by means of a stage micrometer, which is viewed in the same manner as any object would be. The scale must be calibrated for each objective used. The filar micrometer is almost indispensable for measurements of small lengths.

Binocular microscopes are advantageous from several points of view—they give a correct stereoscopic image, they prevent fatigue in prolonged studies, and with a properly constructed camera very satisfactory stereophotomicrographs can be made. Such photographs are vastly superior to the ordinary two-dimensional picture. Binocular attachments are now constructed for use with the standard monobjective microscopes, but are not so satisfactory as the binocular microscope of the Greenough type, which has paired objectives and paired eyepieces. These instruments are exceedingly useful in the chemical laboratory.

Photographic eyepiece attachments make possible the taking of photomicrographs, or an ordinary camera with lens removed may be used. A light-tight connection between camera and microscope is necessary.

Microscopes for use in the chemical laboratory should be provided with polarizing and analyzing Nicols. Very important information is often secured by examinations of substances in polarized light. Special microscopes known as "chemical microscopes" are now available, having such prisms and other useful accessories.

The Electron Microscope.—The limiting factor in the resolution of small objects by the optical microscope is the wave length of the light.

The details of material under examination cannot be seen if they are smaller than the wave length of the light used in the observation. A beam of electrons has many of the properties of a beam of light, and by application of the simple formula

$$Ve = h\nu$$

where V is the applied voltage, e is the charge on the electron, h is Planck's constant, and ν is the frequency of light, it is readily calculated that a beam of electrons can have a wave length of a fraction of an angstrom unit, as against 4,000 to 8,000 Å for the wave length of visible light. Moreover, the electron beam can be bent by an electrostatic or an electromagnetic field so that it can be focused by simple adjustment of current and voltage. These principles have been applied to make practical electron microscopes,[1-3] and many excellent pictures have been taken with them. Whereas a magnification of 2,000 is about the limit of optical microscopes, the useful limit of present-day electron microscopes seems to be a magnification of about 100,000. Theoretically, the wave length of the electron beam is of the order of 1/100,000 that of visible light. Bacteria, fine powders such as carbon black, fibers, and many things of biological interest have been examined with much greater magnification than was previously possible, and new details have been revealed. Particularly in the study of nonfiltrable viruses the method holds promise. Objects 30 Å in diameter can now be photographed.
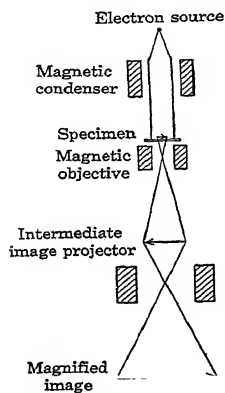
Electron source
Magnetic condenser
Specimen
Magnetic objective
Intermediate image projector
Magnified image
Fig. 73.—Electron microscope.

The principle of the electron microscope is shown in Fig. 73. Electrons are produced as in radio tubes, given velocities of 30,000 to 100,000 volts and focused with magnetic fields as indicated. The object is placed on a thin nitrocellulose film which is fairly transparent to the beam and which shows no structure of its own. The electrons pass through and are focused on a fluorescent plate where the image is viewed by eye. The electrons are scattered by the denser parts of the object but the transparent parts of the object show up more

[1] Bulletin on "The Electron Microscope," Radio Corporation of America Manufacturing Co., Camden, N. J. (1940).

[2] Krause, Das magnetische Electronenmikroskop und seine Anwendung in der Biologie, *Naturwiss.*, **25**, 817 (1937).

[3] Meyers, "Electron Optics," Chapman & Hall, Ltd., London (1939).

brightly. A photographic plate is then substituted for the fluorescent screen, and a short exposure gives a satisfactory picture.

The electrons are easily deflected by the molecules of air, and it is necessary to evacuate the apparatus including focusing chambers, object, and photographic plate to a high vacuum, using a powerful vapor vacuum pump. Special compartments are arranged so that transfer of objects and plates can be made without re-evacuating the whole apparatus.

CHAPTER XIX

SOLUTIONS

Vapor Pressure of Binary Mixtures

The determination of the boiling points of solutions has been described on pages 78 and 82. When one of the components is non-
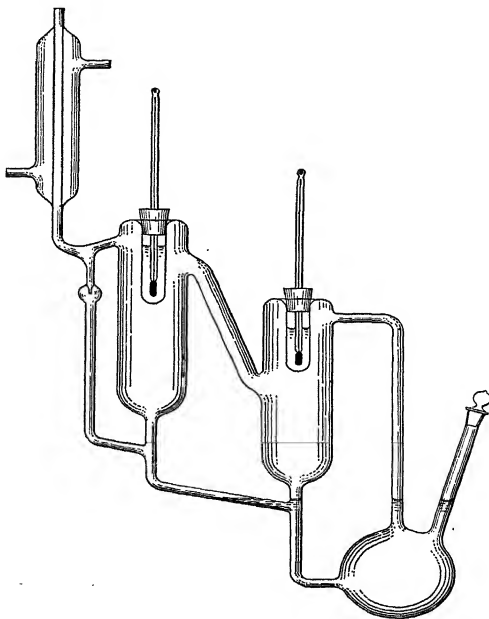
G. 74.—Swietoslawski apparatus for vaporization of binary mixtures.

volatile, as in the experiment described on page 68, the composition of the vapor does not change during distillation. When both components are volatile, the compositions usually change. A knowledge of

the temperatures and the compositions of liquid and condensing vapor is often desired.

The temperature difference between liquid and condensing vapor phase can be obtained more accurately and more easily than the independent determination of each. An effective method for determining this quantity is Swietoslawski's differential ebulliometer, shown in Fig. 74.[1] The principle of the Cottrell vapor pump is used, and the solution in the reservoir flask circulates and sprays over the tube that holds the first thermometer. The solution returns to the heating flask while the vapor passes on and condenses on the tube that holds the second thermometer. This condensed vapor together with any vapor that reaches the reflux condenser is returned to the solution so that the concentration remains constant. The first thermometer gives the boiling temperature of the liquid, and the second gives the boiling temperature of the condensed vapor. In the case of a nonvolatile solute this is the boiling point of the pure solvent. The wells holding the thermometers are filled with oil to improve thermal contact, and a spiral of glass or a rough surface on the vapor side helps to obtain equilibrium conditions.

The drain from the reflux condenser is wide so as not to fill up with liquid and cause a hydrostatic pressure. The quantity of vapor condensing is estimated from the rate at which the drops fall.

This apparatus may be used to test the efficiency of a fractionating column which is placed between the two thermometer wells.

Another differential vapor-pressure device is described by Menzies and Wright.[2] A narrow graduated tube is closed at one end and bent up to give a U tube with the closed arm about 2 cm long and the other arm about 12 cm long. It is partly filled with water or other liquid, sealed off at the ends, and placed vertically in a flask. There is thus an air pocket in the short arm and another one at the top of the long arm. A vapor pump pours the boiling solution over the pocket in the lower arm, whereas the pocket at the top of the long arm is surrounded only by vapor. Measured changes in the level of the enclosed liquid enable one to calculate the differences in vapor pressure of this liquid, and from the differences in vapor pressure the corresponding differences in temperature may be calculated. This temperature difference then is equal to the difference in temperature between the solution boiling in the flask and its vapor. At 35° a difference in level of 1 mm of water corresponds to 0.0313°, and at 100° it corresponds to 0.0026°.

[1] SWIETOSLAWSKI, *J. Chem. Ed.*, **5**, 469 (1928); "Ebulliometry," Jagellonian University Press, Krakow (1936).

[2] MENZIES and WRIGHT, *J. Am. Chem. Soc.*, **43**, 2314 (1921).

A modification of the Swietoslawski apparatus is described by Gilmann and Gross.[1]

The most accurate apparatus for making these determinations is described by Scatchard[2,3,4] and his associates. The best dimensions for the Cottrell pump and the means for accurate control and measurement of pressure and temperature are given. With this apparatus, measurements have been made on several pairs of liquids with an accuracy that permits accurate thermodynamic calculations.

The partial pressures of liquids in a mixture, or the vapor pressure of the solvent when a nonvolatile solute has been added, are needed for calculating activities and thermodynamic quantities. The gas-saturation method described elsewhere is satisfactory. When both components are volatile it is necessary to have a suitable means for analyzing the condensed vapor. A physical method such as refractometry or a chemical method such as titration may be used.

Fractional Distillation[5]

The separation of liquids by distillation has been discussed, and the methods of testing the efficiency of separation have been described on pages 78 and 82.

This efficiency is greatly affected by the type of fractionating column. For practical operation it is desired to meet the following conditions:

1. High efficiency, *i.e.*, a large number of theoretical plates.
2. Small space requirement, *i.e.*, short column.
3. Large throughput, *i.e.*, rapid flow of vapor.
4. Small holdup, *i.e.*, minimum retention of liquid.

If the last two conditions are not met, the column and packing may become flooded. In attempting to meet these requirements many different fractionating columns have been devised, some of which are cited here.

1. Bubble caps (Brunn).
2. Umbrella caps (Young).
3. Glass beads or pearls (Hempel).

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[1] GILMANN and GROSS, *J. Am. Chem. Soc.*, **60**, 1525 (1938).

[2] SCATCHARD, RAYMOND, and GILMAN, *J. Am. Chem. Soc.*, **60**, 1275 (1938).

[3] SCATCHARD and RAYMOND, *J. Am. Chem. Soc.*, **60**, 1278 (1938).

[4] SCATCHARD, WOOD, and MOCHEL, *J. Am. Chem. Soc.*, **61**, 3206 (1939); **62**, 712 (1940).

[5] For further material the following references are recommended: ROBINSON and GILLILAND, "Elements of Fractional Distillation," McGraw-Hill Book Company Inc., New York (1939); MORTON, "Laboratory Technique in Organic Chemistry," Chap. IV, McGraw-Hill Book Company, Inc., New York (1938).

4. Short lengths of glass tubing.

5. Metal chain (Washburn).

6. Carding staples.

7. Carborundum particles on wall (Midgely).

8. Glass helices (Fenske).   .

9. Protrusions poked into wall (Vigreaux).

10. Double cones of metal screen (Stedman) (page 85).

11. Long strip of metal screen twisted into spiral (Lecky and Ewell).

12. Spiral rod between two concentric tubes (Widmer).

13. Spiral of wire or glass against inner wall (Podbielniak)[1] (page 85).

Many of these have special advantages.   Laboratory fractionating columns are available commercially with one to two theoretical plates per inch.   The last six columns seem to be particularly effective.   The last five have a small holdup.   The opportunities for improvement in fractionating columns have not been exhausted, although great improvements have been made in the last decade.[2]

It is essential to keep the walls at the temperature of the vapor to prevent condensation of cold liquid.   An insulating jacket, a vacuum jacket, or an electrically heated jacket may be used.

An effective column with rotating vanes has been devised for the concentration of isotopes,[3] a purpose that calls for a very large number of theoretical plates.

Vapor Pressures by the Isotonic Method

The isotonic method is beautifully simple.   Solutions in several small dishes are merely placed in a closed vessel which is very accurately thermostated, the air is evacuated to facilitate the diffusion of vapor, and the solutions are tested at intervals until they show no further change.   Then all solutions have exactly the same vapor pressure, and the value of this vapor pressure is calculated from a knowledge of the concentration in one of the solutions used as a standard.

Robinson and Sinclair[4] compared the activities of water in solutions of inorganic halides with those of potassium chloride at different concentrations.   Scatchard, Hamer, and Wood[5] determined the activities of water in solutions of potassium chloride, sulfuric acid, sucrose, urea, and glycerol as compared with solutions of sodium chloride.   The

[1] PODBIELNIAK, *Ind. Eng. Cham. Anal. Ed.*, **5**, 119 (1933).

[2] WARD, *U. S. Bur. Mines Tech. Paper* 600 (1939).

[3] UREY and HUFFMAN, *Ind. Eng. Chem.*, **29**, 531 (1937).

[4] ROBINSON and SINCLAIR, *J. Am. Chem. Soc.*, **56**, 1830 (1934).

[5] SCATCHARD, HAMER, and WOOD, *J. Am. Chem. Soc.*, **60**, 3061 (1938).

results are very accurate and permit a check on the several different methods that have been used for the activity of water in solution. This method probably gives more accurate results than any other.

Six metal cups, 3.5 cm. high and 2.5 cm in diameter, are fitted with tight covers for weighing. The cups are filled with different solutions. They fit snugly into holes bored in a large copper block. This block fits into a stainless steel vessel with a cover and lead gasket so that the whole system can be evacuated and rotated in a large thermostat kept constant nearly to 0.001°.

After 24 hr. the little cups are covered and weighed. They are replaced in the vessel, the covers removed, and the determinations repeated again after 24 hr. or until there is no further change in weight.

The massive copper block and very close regulation of the thermostat is necessary to prevent slight irregularities in temperature among the different solutions.

Osmotic Pressure

The simplest device for demonstrating osmosis is an inverted thistle tube with a parchment or an animal membrane stretched across its mouth. When filled with a solution and placed in pure water, the water passes through the membrane into the solution. The hydrostatic pressure developed in the tube is a measure of the osmotic pressure, but equilibrium is reached slowly, and the semipermeable membrane is apt to rupture. It is suitable only for very dilute solutions. For more concentrated solutions, it is necessary to use a supported membrane, preferably in an apparatus in which the pressure is applied on both sides of the semipermeable membrane in order to avoid breakage. In the apparatus of Frazer and Myrick,[1] a porous clay cup contains an electrolytically deposited membrane of copper ferrocyanide, which allows the passage of solvent but not of solute. This clay cup, containing the solvent, is surrounded by a strong bronze cylinder, to which is attached a manometer. The space between the porous cup and walls of the bronze cylinder is filled with the solution whose osmotic pressure is to be determined.

To measure the pressure, an electrical resistance gage or a water interferometer may be used, in place of the customary mercury manometer. With this apparatus Frazer and his coworkers have measured osmotic pressures up to 273 atm.

Measurements of the osmotic pressure of solutions of large molecules are determined with cellophane membranes. The electrolytes

[1] FRAZER and MYRICK, *J. Am. Chem. Soc.*, **38**, 1907 (1916); FRAZER and LOTZ, *J. Am. Chem. Soc.*, **43**, 2501 (1921).

which are difficult to remove would introduce a serious error except for the fact that they pass through the membrane unhindered and thus appear on both sides in equal concentration.   A rise of a few millimeters shows that the particles are of colloid dimensions with molecular weights of several thousand.   The method is of importance in the study of biology and in the study of high polymers and resins.

CHAPTER XX

THERMOCHEMISTRY

Calorimeters

A calorimeter is an instrument for measuring the heat changes in a system. Usually heat is evolved, and the temperature of the water in the calorimeter is raised. The amount of heat evolved is calculated by multiplying the heat capacity of the water together with that of the calorimeter by the rise in temperature.

Although calorimetric measurements are among our most important and oldest measurements, they have not, in general, attained the accuracy afforded by many other measurements in physical chemistry.

Many precautions must be taken, their extent depending on the accuracy demanded. Some of them are discussed below.

1. Efficient stirring of the liquid in the calorimeter is necessary at all times to ensure uniform temperature. To prevent excessive heating, the bearings are well above the calorimeter so that there can be no heat generated by friction or mechanical contact.

2. Evaporation is eliminated, or else a correction is applied for the heat lost through evaporation. It may be practically eliminated by placing a thin metallic cover over the calorimeter or by using an adiabatic calorimeter in which the temperature of the jacket water is raised so as to keep pace with that of the calorimeter.

3. As the temperature rises, heat is radiated to the colder surroundings, and a correction is made for this radiation loss, or, better, the radiation is prevented by experimental means. If a correction is to be made, the best results are obtained with a jacket kept at constant temperature.

4. Convection currents of air from a warm calorimeter to a colder jacket are made as small as possible, or they are kept uniform to permit a proper correction. The adiabatic method eliminates them.

5. The heat capacities of the calorimeter and accessories are small and absolutely constant, so that they will be the same during experimental determinations as during calibration. The depth of immersion of the thermometer and stirrers should always be the same, and opportunities for irregular thermal leakage should be reduced to a minimum.

6. The thermometer is read carefully, because the percentage accuracy of the result can be no greater than the percentage accuracy of the temperature reading. Standardized thermometers are necessary.

The whole field of calorimetric precision and the errors in calorimetry have been discussed in great detail by White.[1]

The simplest calorimeter making use of a vacuum-jacketed bottle has been described on pages 103 and 109. It is entirely satisfactory for most work in which an accuracy to within 1 or 2 per cent is sufficient.

For more accurate work, a metal-walled calorimeter is used in which the heat capacity of the calorimeter is more sharply defined, thus giving more reproducible cooling corrections.

The general plan of such calorimeters is shown in Fig. 75. The reaction evolving the heat is arranged to take place within a container immersed in the water of the inner vessel.

Evaporation is minimized by placing over the calorimeter a thin metallic cover which is in good thermal contact with the water of the calorimeter. A pad of insulating material may be placed over it to minimize radiation.

FIG. 75.—Metal-walled calorimeter.

The water in the jacket is thermostated and kept well stirred, and the water in the calorimeter is circulated with a propeller which lifts the water up through a tube. The height of the can is usually 50 per cent greater than the diameter. An air gap of about 1 cm has been found to give the optimum conditions of reduced radiation and convection. A thin metallic cylinder in the center of the air gap can be used to reduce further the convection losses. Under these conditions, the heat losses are definitely controlled, and a satisfactory correction can be applied. The calorimeter proper is set into a slightly larger can, placed on small supports of cork or glass tubes slipped over projecting studs which are soldered to the outer vessel.

Still better results may be obtained by immersing the whole calorimeter in the jacket water, using a tightly fitting cover. A brass cover with large coarse threads is screwed on the can, and it is rendered watertight by smearing the threads with a heavy coating of white lead. The white lead is wiped off after a determination, to prevent sticking of
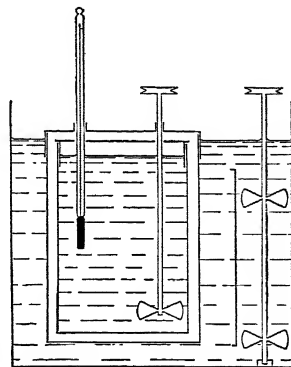
[1] WHITE, "The Modern Calorimeter," Reinhold Publishing Corporation, New York, (1928).

the cover; or the joint between cover and can may be made by means of a rubber gasket and small clamps.

Glass tubes for thermocouples and leads are sealed to the cover with de Khotinsky cement, or pass down through brass tubes soldered into the cover. They extend above the level of the water in the jacket. For higher temperatures, they are set in a packing of graphitized asbestos, which is screwed down tightly.

A very satisfactory stirrer is a propeller driven by a motor. The blades are surrounded by a vertical tube open at the top and bottom, and in this way water is lifted continuously from the bottom to the top. Obviously, this type cannot always be used, and vertically oscillating stirrers are often adequate.
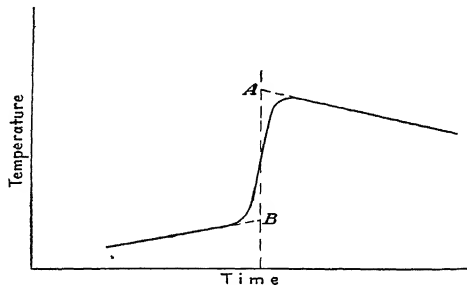
FIG. 76.—Graphical method for cooling correction. *AB* represents the corrected rise.

The heat of stirring is kept as small as possible; the stirrer turns freely without touching the sides, and the bearings are well outside the calorimeter. The stirring in the jacket is vigorous, and the heat generated does no harm. The jacket stirrer operates in a small cylindrical compartment attached to the side, with openings at the top and bottom.

The stirring may be accomplished without moving parts by bubbling a fine stream of air through a coarse capillary with an outlet at the bottom of the calorimeter.[1] The calorimeter is placed in a thermostat, and the incoming air is passed through water and through a copper coil in the thermostat so that it will be saturated. In this way there is no heat effect due to vaporization or condensation in the calorimeter, and the mechanical generation of heat is very small.

In making the cooling correction the temperature is read every minute for 5 or 10 min. before the reaction, and again for about 10 min. after the temperature has appeared to reach a maximum. The tem-

[1] CAMPBELL and CAMPBELL, *J. Am. Chem. Soc.*, **62**, 291 (1940).

peratures are plotted against time, and an ordinate is drawn at a time midway between the time of starting the reaction and the time of maximum temperature. The curves representing the temperatures before and after the reaction are then extrapolated to this line, as shown in Fig. 76. The vertical distance AB between these two intersections is taken as the temperature rise.[1]

Adiabatic Calorimeter.—In the adiabatic calorimeter devised by Richards, the temperature of the jacket is raised at such a rate that its temperature is always equal to that of the inner calorimeter. A cooling correction is then unnecessary. Careful adiabatic control to about a tenth of a degree is usually necessary to eliminate all corrections; a poorly controlled adiabatic calorimeter is less satisfactory than a nonadiabatic calorimeter with the accompanying cooling correction.

Richards heated the jacket water by mixing acid and alkali, but electrical heating is more convenient. An electric heating coil may be used if the liquid in the jacket is light oil or other nonconducting liquid. Good results are obtained by passing an alternating current directly through the water (containing a little electrolyte). This scheme necessitates the adoption of certain dimensions to ensure a fairly even liberation of heat throughout the liquid in the jacket. The time lag in heating is eliminated by this electrolytic heating.[2]

The inner vessel is set into a large can with a watertight cover. This can is supported in a larger jacket, on glass (or, better, bakelite) tubes which are slipped over brass rods soldered to the jacket. The jacket is connected to one wire and the can to the other, so that alternating current passes directly through the water. The adiabatic control is governed by a thermel, and the current is passed through the jacket as needed to keep the galvanometer at zero deflection, indicating that both calorimeter and jacket are at the same temperature. The operation can be made automatic with a photoelectric cell and suitable relay system. Care is necessary to avoid electrical shocks.

Isothermal Calorimeter.—It is possible to measure the evolution of heat under conditions where there is no temperature change and the heat capacity of the material and the calorimeter are not involved. The Bunsen ice calorimeter measures the heat evolved by finding the quantity of ice melted. As the ice melts, the volume decreases and mercury is sucked out of a weighed dish.[3] For each gram of liquid

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[1] More elaborate cooling corrections are discussed by White (reference 1).

[2] DANIELS, *J. Am. Chem. Soc.*, **38**, 1473 (1916); WILLIAMS and DANIELS, *J. Am. Chem. Soc.*, **46**, 903 (1924).

[3] BUNSEN, *Pogg. Ann.*, **141**, 1 (1870); RICHTER, *Z. Instrkde.*, **32**, 177 and 234 (1912).

water produced, 79.63 cal. are evolved. In a similar manner, the vapor calorimeter measures the quantity of heat evolved by the amount of liquid evaporated at the boiling point. Water, ether, or other liquids may be used.

These calorimeters are limited to one temperature. Slightly different in operation is a calorimeter[1] in which the heating effect is exactly counterbalanced by evaporation of carbon tetrachloride in a stream of air. The carbon tetrachloride evaporated is adsorbed on silica gel and weighed, and the heat corresponding to 1 mg is determined by calibration with an electric heating coil. Two vacuum bottles immersed deep in a thermostat are connected with a thermel, one acting as a reference of constant temperature and the other changing in temperature with the reaction which is being measured. Air is passed through the carbon tetrachloride as needed, to keep the galvanometer at zero, thus ensuring that the measured heat absorbed is exactly equal to the heat evolved in the reaction. Heat developed by slow reactions evolving only 1 cal. per hour may be measured with this calorimeter over a period of several hours.

Heat of Combustion

The combustion calorimeter has been used more than any other, because combustion reactions are rapid reactions capable of accurate thermal measurement and because the heats of oxidation of fuels and foods are of technical importance. It is necessary to ensure complete combustion to the highest state of oxidation, and for this purpose the combustion is carried out in an atmosphere of compressed oxygen. Heavy metal bombs are necessary to withstand the explosion, and they must be of a steel alloy capable of resisting corrosion by the nitric acid produced from the nitrogen of the air by the high temperature of the explosion. The Parr calorimeter with its adiabatic gas-heated hot-water jacket and the Emerson calorimeter with its electrolytically heated jacket are described on page 99.

Many precautions must be followed if an accuracy greater than a few tenths of a degree is to be achieved. These have been discussed by Parks and by Huffman.[2,3] Platinum wire is used instead of iron on account of the oxidation correction of the latter, and the electrical energy required for ignition is determined by measurements of time, current, and voltage. If the sample is a pure organic material, a small platinum cup is used. The fine platinum wire ignites a short

[1] Coon and Daniels, *J. Phys. Chem.*, **37**, 1 (1933).

[2] Richardson and Parks, *J. Am. Chem. Soc.*, **61**, 3543 (1939).

[3] Huffman and Ellis, *J. Am. Chem. Soc.*, **57**, 41 (1935).

length of cotton string which in turn ignites the weighed material in the cup. A platinum resistance thermometer gives temperature differences down to 0.0001°. The corrected rise is calculated by the method of Dickinson.[1] The correction for the oxidation of nitrogen during the explosion may be reduced from about 10 cal. to about 1 cal. under the conditions of this experiment if the air initially present in the bomb is swept out by introducing oxygen to 5 atm., releasing to 1 atm., charging to 5 atm., and again releasing before bringing the oxygen pressure up to 20 atm. One milliliter of water is added to the bomb.

Benzoic acid supplied by the National Bureau of Standards is used for standardizing the bomb calorimeter. The calorimetric conditions are specified by Washburn,[2] and the value of 26,419 international joules or 6315.3 cal. (1 calorie = 4.1833 joule) per gram is taken.[3]

Heat of Reaction

In addition to data on the heats of combustion, other important work is being published in thermochemistry which should be consulted by those intending to undertake precise calorimetric measurements.

Kistiakowsky and his coworkers[4] have determined with great accuracy the heat of addition of hydrogen, hydrobromic acid, and bromine to unsaturated organic compounds.

Gucker[5] and Lange and Robinson[6] have made accurate measurements on the thermal properties of solutions.

Sturtevant[7] has measured carefully the heat of slow reactions and reactions in solution.

The slight heat effects accompanying photochemical reactions have been measured with a photocalorimeter.[8]

As in all work, the chemical purity of the material being measured may easily be the limiting factor in the accuracy of the results.

Heat of Vaporization

The heat required to vaporize 1 g of liquid can be determined most accurately by measuring the electrical energy consumed in evaporating

[1] DICKINSON, *Bull. Bur. Standards*, **11**, 189 (1914).

[2] WASHBURN, *Bur. Standards J. Research*, **10**, 525 (1933).

[3] JESSUP and GREEN, *Bur. Standards J. Research*, **13**, 469 (1934).

[4] KISTIAKOWSKY and coworkers, *J. Am. Chem. Soc.*, **59**, 831 (1937) and earlier papers; **60**, 440 (1938).

[5] GUCKER and coworkers, *J. Am. Chem. Soc.*, **62**, 1464, 2698 (1940).

[6] LANGE and ROBINSON, *Chem. Rev.*, **9**, 89 (1931); ROBINSON, *J. Am. Chem. Soc.*, **55**, 4733 (1931).

[7] STURTEVANT, *J. Am. Chem. Soc.*, **59**, 1528 (1937); **62**, 584, 3519 (1940).

[8] MAGEE, DEWITT, COOLIDGE, and DANIELS, *J. Am. Chem. Soc.*, **61**, 3622 (1939).

a given quantity of the liquid at its boiling point. The apparatus shown in Fig. 77 has been used by Mathews[1] in the accurate determination of heats of vaporization. The inner container filled with purified liquid is suspended from a balance arm and is surrounded with the vapor of the boiling liquid. The electrical energy necessary to vaporize exactly 1 g is determined with a potentiometer, a standard resistance, and a stop watch.

According to another method, a weighed quantity of liquid is condensed from the vapor state in a calorimeter, and the heat evolved by the condensation of the vapor is measured.[2] Premature condensation may cause errors in this method, unless corrections are made.
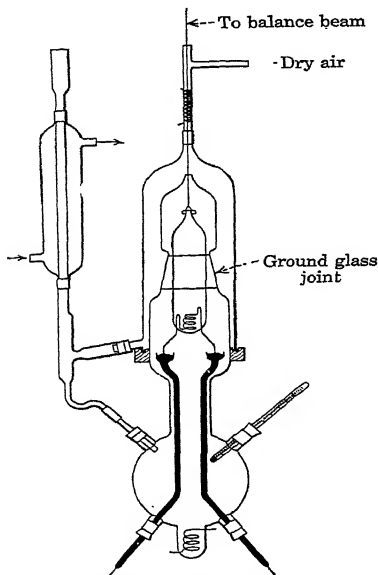
FIG. 77.—Mathews apparatus for measuring heats of vaporization.

Heat Capacity

The heat capacity of liquids and solids is conveniently determined by measuring the amount of electrical energy required to raise the temperature through 1°. A knowledge of the heat capacities down to the absolute zero is valuable for calculating thermodynamic properties and chemical equilibria. In the calorimeter developed by Nernst a wire embedded in the material functions as both heating coil and resistance thermometer. Extensive measurements of specific heats of organic compounds have been made by Parks[3] in a calorimeter in which the material is placed in a can with metal vanes, and a cover is soldered on. The remaining space in the calorimeter is then evacuated, and the temperature after heating for short periods of time is measured with a calibrated thermel.

[1] MATHEWS, *J. Am. Chem. Soc.*, **48**, 562 (1926); **53**, 3212 (1931).
[2] RICHARDS and MATHEWS, *J. Am. Chem. Soc.*, **33**, 863 (1911); MATHEWS, *J. Phys. Chem.*, **21**, 536 (1917).
[3] PARKS and coworkers, *J. Phys. Chem.*, **30**, 47 (1926); *J. Am. Chem. Soc.*, **60**, 1507 (1938), and earlier papers.

Excellent measurements have been made down to low temperatures by Giauque[1] and by Aston.[2]

Many determinations have been made on the heat capacity of organic liquids and aqueous solutions at room temperatures. A calorimeter of the general type shown on page 343 is usually used with an electric heating coil and mechanical stirrer.

Twin calorimeters with thermocouples have been used, one calorimeter containing pure water and the other a salt solution. Richards and Gucker[3,4] describe an accurate calorimeter of this type, and give several references.

An interesting application of the Joule-Thompson effect to liquids permits accurate measurements of the heat capacity of liquids by the piezo method.[5]

The specific heats of gases are so low that a closed system cannot advantageously be used on account of the comparatively large heat capacity of the containing vessel. A flow method involving larger quantities of gas is necessary.

In one method, a certain quantity of heat is supplied to the gas stream as it passes a heating coil, and the temperature before and after being heated is measured with thin wires in the gas stream, operating as resistance thermometers. One of the best of these researches is described by Scheel and Heuse.[6]

In another method,[7] the gas, in a steady stream, is passed through a coil in a thermostat and thence through a small coil in a calorimeter at a higher temperature. The cooling effect caused by the passage of the colder gas is offset by heat supplied from an electric heating coil so regulated that the temperature remains constant. Several adjustments of the current may be necessary before the two effects exactly counterbalance each other; then the electrical heat added is exactly equal to the heat absorbed by the gas. The heat divided by the temperature difference between thermostat and calorimeter and by the weight of gas passing through gives the specific heat capacity of the gas. A correction must be made for the thermal leakage between calorimeter and thermostat, and this correction is large.

[1] GIAUQUE and coworkers, *J. Am. Chem. Soc.*, **60**, 1389 (1938), and earlier papers.

[2] ASTON and coworkers, *J. Am. Chem. Soc.*, **62**, 886 (1940), and earlier papers.

[3] RICHARDS and GUCKER, *J. Am. Chem. Soc.*, **47**, 1876 (1925).

[4] GUCKER and AYRES, *J. Am. Chem. Soc.*, **59**, 447 (1937), and earlier papers.

[5] BURLEW, *J. Am. Chem. Soc.*, **62**, 681, 696 (1940).

[6] SCHEEL and HEUSE, *Ann. Physik*, **37**, 79 (1912); **59**, 86 (1919).

[7] McCOLLUM, *J. Am. Chem. Soc.*, **49**, 28 (1927).

The subject of the specific heats of gases is discussed by Partington and Shilling.[1]

Measurement of Electrical Energy

The input of electrical energy in calorimetry can be measured very accurately, more accurately in many cases than is justified by the other errors in the measurement. The general arrangement is indicated in Fig. 78.
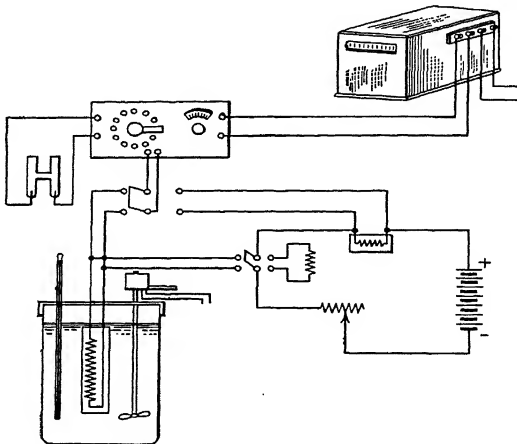
Fig. 78.—Measurement of electrical energy in calorimetry.

The energy in joules dissipated by the heating coil is obtained by multiplying the potential drop across the coil by the current in amperes and the time in seconds. The current is measured by determining the potential drop across a known resistance, placed in series. The current and voltage drop are maintained constant by experimental control throughout the experiment.

The heating coil is made of manganin or other resistance wire having a low temperature coefficient. It may be wound on mica, insulated between two mica sheets, and encased in a silver or copper sheath. In another type of heater the resistance wire is coiled in the form of a spiral and enclosed in a thin glass tube.

The current is supplied by steady storage batteries, in good condition. The standard resistance consists of uncovered manganin

and Shilling, "The Specific Heats of Gases," Ernest Benn, Ltd., London (1924).

or constantan wire or other alloy having a negligible temperature coefficient of resistance. It is immersed in oil to keep the temperature nearly constant, and it should be proved that the current used in the experiment does not raise the temperature of the wire sufficiently to change its resistance. Any excessive heating effect may be reduced by using wire of larger diameter and greater length. The resistance of the standard should be about the same as that of the heating coil, which in turn is designed to give the desired rate of temperature rise.

The potentiometer is used to measure the potential drop across the heater or across the standard resistance. It is not permissible to use a voltmeter, because the voltmeter itself carries some current, and acts as a shunt around the resistance which is being measured. A voltmeter may be used, however, in a compensation method, if it is used with a galvanometer (page 202).

The double-pole double-throw switch connects the potentiometer either to the heating coil or to the standard resistance. It must be of good quality, with perfect contacts and no electrical leakage across the base.

The standard cell, galvanometer, lamp, and scale are accessories for the potentiometer.

The current is kept constant by continuous operation of the rheostat. It is important to have the contacts of the rheostat in good condition. They should be rubbed with emery paper frequently and coated with vaseline. Two rheostats are convenient, one for coarse adjustments and one for fine adjustments. A good rheostat for fine adjustments can be made by changing the level to which an amalgamated resistance wire is immersed in a vertical tube of mercury.

If plenty of batteries are available, it is well to use a large number and bring the current down with a high resistance. In this way, any slight change in the resistance of the circuit has an effect on the current. The circuit is closed by throwing the upper double-pole double-throw switch to the left. Before starting a determination, the lower switch is thrown to the right for several minutes, so that the current will flow through a resistance, which is approximately equal to the resistance of the heating coil. In this way, the battery reaches a steady condition before the experiment is started. If the switch is thrown immediately to the left from the position of open circuit, the battery voltage drops rather rapidly at first and renders difficult the control of the current at a constant amperage. The calculation is simplified, and the accuracy is increased, if the current is kept constant throughout the experiment.

The time of passage of the current is determined with a stop watch or an electric clock or timer. If the time, as measured with a stop watch, is the least accurate factor, a chronograph may be used, or the time may be increased by decreasing the rate of heating. Stop watches used for such work should be checked frequently, as they are likely to get out of order.

All connections should be soldered, using rosin flux. For precision work, an equipotential shield is provided to eliminate stray currents. All the instruments are set on a piece of sheet metal, which is grounded, and under every insulator is placed a grounded metal shield.
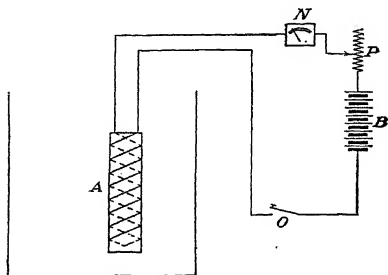
Fig. 79.—Simplified system for measuring the input of electrical energy.

A considerably simpler apparatus for measuring the input of electrical energy is shown in Fig. 79. It is less accurate, but the errors, amounting to perhaps 1 per cent, are not too great for many purposes. The potentiometer is dispensed with, and the current is measured with an ammeter N. Current is supplied to the heater A from a storage battery B, through the simple switch O and the ordinary rheostat P. The potential drop across the heating coil is calculated from the current and the resistance of the coil, the latter being measured with a Wheatstone bridge. The heater is made of manganin or other alloy having a low temperature coefficient of resistance, and an overload is avoided so that the resistance measured at room temperature will be very nearly the true resistance under working conditions. With ordinary wire and a heavy current the resistance will be considerably higher than at room temperature. The resistance when the current is flowing is determined by measuring the voltage drop with a potentiometer as previously described.

The energy input in joules is obtained by multiplying the resistance of the coil in ohms by the square of the current in amperes and the time in seconds.

CHAPTER XXI

COLLOID CHEMISTRY

Apparatus for Preparation of Colloids

Colloids are prepared by either of two general methods.

1. By subdividing coarse material—the dispersion methods.

2. By gathering atoms, molecules, or smaller particles together —the condensation methods.

There are several instruments of commercial and laboratory importance which make use of these principles.

The Colloid Mill.—New developments in the preparation of stable technical emulsions have become possible with the advent of colloid mills. There are at least three types of mill. One of them, of which the Plauson mill is an excellent example, depends upon disintegration by impact, the shock being transmitted through a liquid. Another type operates by hydraulic shear. In the Premier mill, the rotor consists of a perfectly smooth face upon the frustum of a cone, working in accurate and very close relation to a similarly ground surface of a stator. In operation, a centrifugal pumplike effect is set up, and the mixture is drawn through the mill in a continuous manner. The speed of the rotor plate may reach 20,000 revolutions per minute. In some forms of this type of mill, the rotor plate carries a few radial V-shaped grooves to assist the material to pass through the mill. Also, in some mills there are two rotors (no stator) rotating in opposite directions.

The Kek mill represents the third type. A horizontal rotating disk is provided with studs and runs coaxially against a superimposed stator disk, which is also provided with studs. Liquids enter through the center of the stator, with discharge of the emulsion taking place at the circumference, where the distance between the disks is smallest.

Complete descriptions of the various types of mill are to be found in a monograph by Travis.[1]

The Homogenizer.—This instrument consists of a conical agate valve which has been carefully ground to fit a seat. The valve closes by means of a very strong spring. The pressure of the spring is so great that the emulsion must be pressed against the valve by means of

[1] TRAVIS, "Mechanochemistry and the Colloid Mill," Reinhold Publishing Corporation, New York (1928).

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a pump.   The valve opens only to a slight extent so that the drops of the emulsion which pass through are greatly reduced in size.

Other homogenizers depend for their action on the breaking up of suspended droplets by impact when a high-velocity jet of the liquid is forced against a baffle plate.   The homogenizer finds considerable use in the dairy industry.

Supersonic Oscillator.—These oscillators, useful in the preparation of emulsions, aerosols, etc., consist of two units, a high-voltage rectifier

OSCILLATOR UNIT
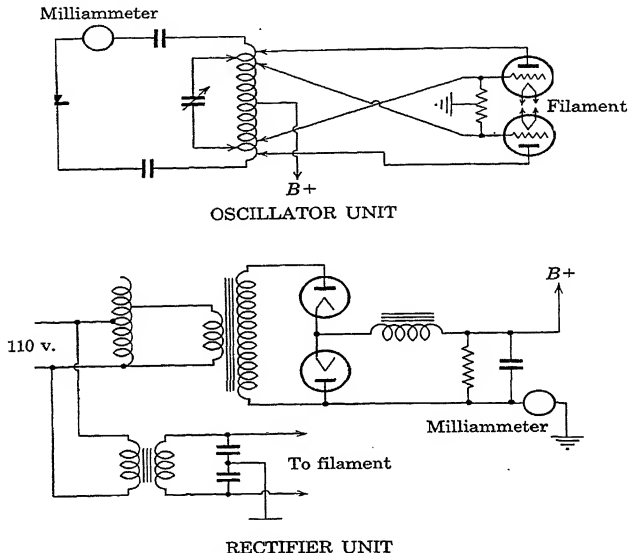
RECTIFIER UNIT
FIG. 80.—Circuit for supersonic oscillator.

and an oscillator which motivates a quartz crystal immersed in a dielectric fluid.   A useful laboratory model has been described by Porter.[1]

Rectifier and oscillator circuits are shown in Fig. 80.

Electric Arc Methods.—The condensation processes are of greater importance.   Certain of these processes are purely chemical in nature, requiring only chemicals and ordinary clean glassware, whereas others require elaborate apparatus.   A condensation method, of considerable importance in the preparation of colloidal solutions, is that of the

[1] PORTER, *Ind. Eng. Chem. Anal. Ed.*, **12,** 748 (1940).

electric arc. By this means, a number of metals are readily evaporated and later condensed within the liquid which serves as the dispersion medium. The electric-arc method was first suggested by Bredig,[1] but has received its greatest development in the hands of Svedberg.[2] For simple arcs, either alternating or direct current may be used. The simpler forms of arc do not give uniform colloids of high dispersivity.

To remedy this defect, Svedberg has devised methods by which sols of greater purity and concentration may be obtained. One such scheme is to protect the electrode surface from the cooling action of the liquid and to avoid decomposition of the dispersion medium by enclosing the arc in a silica tube. Another and still more successful method is to produce the sol by means of the oscillatory arc. The latter is produced by means of an induction coil, low-frequency transformer, or Tesla coil. The circuits used and analyses of the sols that have been produced are described in detail by Svedberg.

Miscellaneous.—Adiabatic expansion, lowering of the temperature of the system, solvent change, and addition of electrolyte to produce fractional salting-out are other condensation methods used in the preparation of colloidal systems.[3]

Apparatus for Purification of Colloids

The purification of a colloid, in its ordinary sense, means the removal of electrolytes from it. The simplest method of separating electrolytes from a colloid is that of dialysis. The dialyzer consists of a membrane through which electrolytes may pass freely but behind which the colloid is retained. A very practical dialyzer can be set up by immersing a collodion bag, containing the colloid to be purified, in a beaker of water. To facilitate the removal of the ions, the water must be continually changed. The collodion bags are formed on the inside of suitably sized test tubes or Erlenmeyer flasks and are removed by soaking them with water after the ether and alcohol have almost completely evaporated. Care must be taken that the bags do not dry too completely at the mouth of the tube or flask; much trouble can be avoided by loosening the collodion from the edge before it has completely dried. These membranes can be made with pores of different sizes, according to the concentration of the collodion solution used in their preparation and the number of thicknesses of collodion used. Some sausage casings are extremely useful in dialysis.

[1] BREDIG, *Z. angew. Chem.*, **41**, 951 (1898); *Z. physik. Chem.*, **32**, 127 (1900).

[2] SVEDBERG, "Colloid Chemistry," 2d ed., Reinhold Publishing Corporation, New York (1928).

[3] COHN, *et al.*, *J. Am. Chem. Soc.*, **62**, 3396 (1940).

Ordinarily dialysis is a slow process. The development of electro-dialysis has made it possible not only to reduce considerably the time necessary to purify a colloid, but also to remove the last traces of electrolytes from certain systems from which this was not possible with the simple dialyzer, without the introduction of complicated apparatus. A collodion sack, partly filled with the colloid, is lowered into a cell containing water and a positive and negative electrode, with (ordinarily) 100 to 200 volts potential difference between them. The cations and anions within the membrane are attracted to the cathode and anode of the cell, their removal being accelerated by the driving force of the applied voltage.

If it is necessary to remove nonelectrolytes from a colloid, the process of ultrafiltration must be resorted to. This process is essentially a filtration by pressure, by which particles between certain sizes may be separated, using membranes of different sizes.

McBain and Kistler[1] recommend the use of cellophane as membrane material for ultrafiltration, and methods of grading the pore sizes are given. Bauer and Hughes[2] have presented a complete and detailed discussion of the preparation of gradocol membranes. The original method of Elford[3] has been improved in important respects.

Sedimentation Apparatus

In sedimentation experiments it must be noted that observations can be made either of the equilibrium condition or of the velocity with which a particle moves in a gravitational field, and care must be exercised that the two are not confused. These sedimentations may take place under the influence of the gravitational field of the earth, or of a centrifuge.

In the equilibrium method, it is necessary to determine the distribution of concentration with height after equilibrium has been attained. In his well-known studies, Perrin[4] used a sedimentation cell, which was only 0.1 mm in height, and made counts of the number of particles at several different levels within it, using a microscope. These measurements were made with particles of known size in order to determine the Avogadro number. Westgren[5] later used the same method to determine the size of suspended colloidal particles, for the value of the

[1] McBain and Kistler, *J. Gen. Phys.*, **12**, 187 (1928); *Trans. Faraday Soc.*, **26**, 157 (1930); *J. Phys. Chem.*, **35**, 130 (1931).

[2] Bauer and Hughes, *J. Gen. Phys.*, **18**, 143 (1934).

[3] Elford, *J. Path. Bact.*, **34**, 505 (1931).

[4] Perrin, *Compt. rend.*, **147**, 530, 594 (1908); **152**, 1165, 1380 (1911).

[5] Westgren, *Z. physik. Chem.*, **89**, 63 (1915).

Avogadro number was known with a considerable degree of accuracy at this time. In order to avoid the difficulties involved in a slow attainment of equilibrium, Svedberg[1] developed an ultracentrifuge for low and medium centrifugal forces and has achieved remarkable success in the determination of the molecular weights of a number of proteins. This method should be applicable to particles of all shapes.

A measurement of the velocity with which a spherical particle sediments also permits the calculation of the particle size or weight. For larger particles, the time of fall through a given distance may be observed directly. For suspensions and solutions of proteins, high-speed oil-turbine ultracentrifuges, also developed by Svedberg[1] and his associates, have been very successful. Centrifugal forces greater than 400,000 times the force of gravity have been attained. In the cases of nonspherical molecules, the weight or size of a molecule cannot be determined from either the diffusion constant or the sedimentation velocity alone, but a combination of the two gives a satisfactory result when proper allowance is made for the effect of concentration upon each.

Air-driven ultracentrifuges of several types, for concentration as well as for analytical purposes, have been developed in this country by Beams, Bauer, McBain, Wyckoff, and others.

Sedimentation experiments also make it possible to determine the size-distribution curve of the colloidal system. Thus Oden[2] has devised an apparatus by which it was possible to record automatically the amount of sediment collecting on a plate immersed in the suspension and hung on one arm of an analytical balance. Other types of sedimentation apparatus for this purpose are also available.[3]

Diffusion Apparatus

Another method for testing the validity of the application of the molecular kinetic theory to colloidal systems is to study the diffusion process. The apparatus required is, as in the case of the sedimentation apparatus, simple in principle, but rather complicated in detail. A diffusion cell used by Svedberg[4] is shown in Fig. 81. More recently a

[1] Svedberg and Pedersen, "The Ultracentrifuge," Clarendon Press, Oxford, 1940; Svedberg, *Proc. Roy. Soc.* London, **A170**, 40 (1939); *Ind. Eng. Chem. Anal. Ed.*, **10**, 113 (1938).

[2] Oden, in Alexander, "Colloid Chemistry," vol. I, Reinhold Publishing Corporation, New York (1926).

[3] Ostwald and Hahn, *Kolloid-Z.*, **30**, 62 (1922); Kelly, *Ind. Eng., Chem.*, **16**, 928 (1924); Kraemer and Stamm, *J. Am. Chem. Soc.*, **46**, 2710 (1924).

[4] Svedberg, "Colloid Chemistry," 2d ed., p. 141, Reinhold Publishing Corporation, New York (1928).

diffusion vessel with plane-parallel windows and requiring not over 2 ml of solution has been designed by Lamm.[1]   It is shown in Fig. 82. Such cells must be carefully protected from any external vibrations and from any change in temperature.   The boundary between diffusing solution and solvent is illuminated by means of suitable lamps, so that a picture of the diffusing column can be taken from time to time with a camera.   If colorless substances are diffusing, the blurring of the boundary is followed by light absorption or by refractometric methods.   Included in the latter are the various modifications of the Toepler Schlieren method (Philpot, Svensson, Longsworth, *et al.*).   Another diffusion cell which requires a small amount of solution has been described by Stamm and Loughborough.[2]

The diffusion cell of Fürth and Ullmann,[3] for experiments under the microscope, is ingenious in
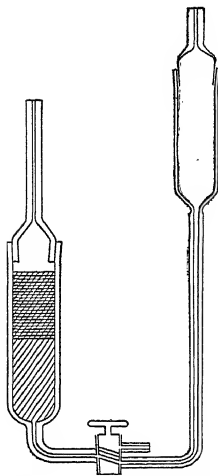
FIG. 81.—Svedberg diffusion cell.
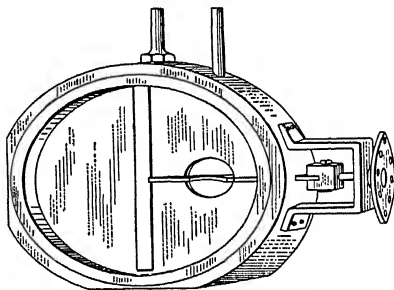
FIG. 82.—Lamm diffusion cell.

principle and should be capable of wide adaptability.   The principle upon which it depends is illustrated by Fig. 83.   The cell *C*, built on a microscope slide, is divided into two parts by the wall *W*.   The left-hand compartment is further divided by a bar *B*.   A dye solution is placed in part *D*, below the bar, and above the bar is placed a layer of the pure solvent.   To start diffusion, the bar *B* is removed by an electromagnetic arrangement, indicated by *M*.   A dilute solution of the dye is placed in compartment *A* to the right of the wall, to serve as a colorimetric standard, and the diffusion is followed with a movable microscope.

[1] Lamm, Dissertation, Upsala (1937); Polson, *Kolloid-Z.*, **87**, 149 (1939).
[2] Stamm and Loughborough, *J. Phys. Chem.*, **40**, 1113 (1936).
[3] Fürth and Ullmann, *Kolloid-Z.*, **41**, 300 (1927).

Other forms of apparatus for diffusion studies are described by Williams and Cady.[1]

Electrokinetic Apparatus

Apparatus for electrophoresis experiments has taken a number of more or less complicated forms, all of which are modifications of the
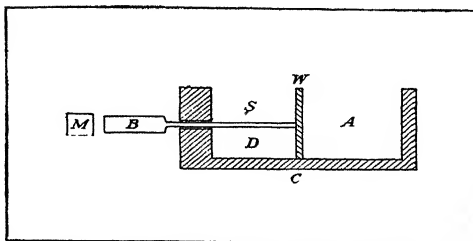
Fig. 83. Fürth diffusion cell for microscopic observations.
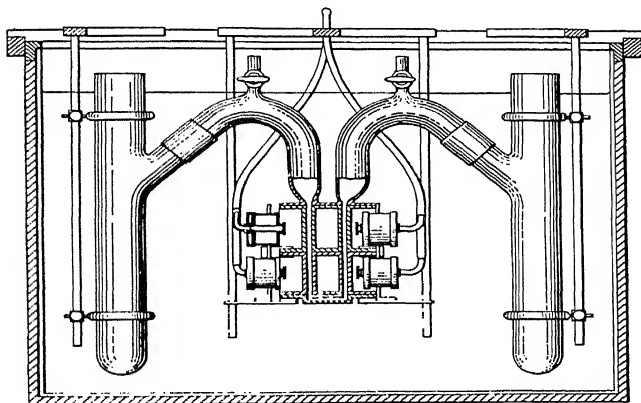
Fig. 84.—Tiselius electrophoresis cell.

simple instrument used by Burton. The new Tiselius apparatus is shown in Fig. 84. Improvements have been designed to make possible more exact determinations of the movements of the boundaries,[2] to

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[1] WILLIAMS and CADY, *Chem. Rev.*, **14**, 171 (1934).

[2] LAMM, *Z. physik. Chem.*, A **138**, 313 (1928); A **143**, 177 (1929).

decrease or eliminate the disturbing influence of electrode reactions, to prevent convections,[1] and to make more exact computations.[2]

Simple but quite accurate ultramicroscopic methods of observing the migration of single colloidal particles are due to Mattson[3] and to Abramson.[4] A diagrammatic reproduction of the Mattson cell is given in Fig. 85.
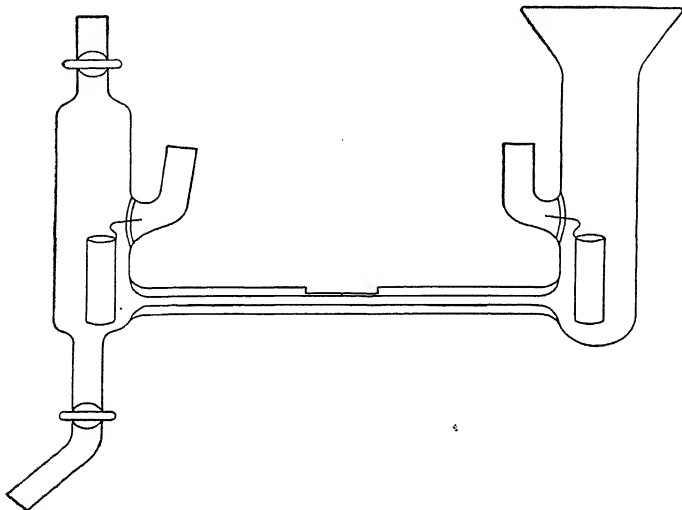
Fig. 85.—Mattson electrophoresis cell for use with ultramicroscope.

The theory of electrokinetic phenomena has recently been reviewed by Horwitz.[5]

Optical Apparatus

The Ultramicroscope.—The optical methods of colloid chemistry have given much information concerning the size, shape, and structure of particles.   Any particle having a diameter less than 120 μ cannot be observed directly with a microscope.   However, any particle down to 5 μ can be caused to reflect light if it is not too close to other par-

[1] Tiselius, *Trans. Faraday Soc.*, **33**, 524 (1937).

[2] Longsworth and MacInnes, *J. Am. Chem. Soc.*, **62**, 705 (1940).

[3] Mattson, *J. Phys. Chem.*, **32**, 1532 (1928).

[4] Abramson, "Electrokinetic Phenomena," Reinhold Publishing Corporation, New York (1934).

[5] Horwitz, *J. Chem. Ed.*, **16**, 519 (1939).

ticles. The ultramicroscope is an instrument in which the particles are very strongly illuminated, and they are observed with a microscope so that as much light as possible from each particle is received in the eye. In the figure (Fig. 86), a strong source of light A is focused by means of a lens L on the slit S, which is so constructed that it may have either a horizontal or vertical position with respect to the base. The light is again focused on the cell C, which contains the diluted colloid, by means of a lens L' and an objective O. An ordinary microscope M is used to observe the light scattered by the particles of the colloid. This is essentially the ultramicroscope described by Siedentopf and Zsigmondy[1] and is commonly known as the "slit ultramicroscope."
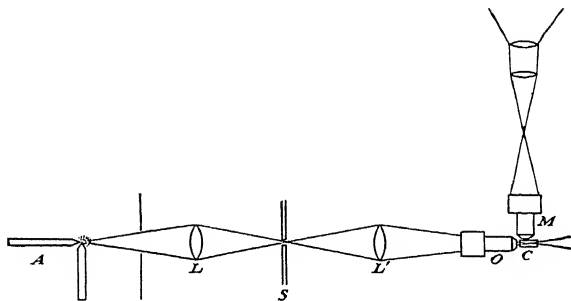
Fig. 86. Principle of the ultramicroscope.

Siedentopf gives four factors that control the efficiency of the ultramicroscope:

1. The source of light should be as strong as possible.

2. The aperture of the illuminating system and the system used for observing the particles should be as high as possible.

3. There must be high contrast between the particles and their background.

4. The light-emitting power of the particles should be high.

The cell proper, in which the colloid is observed, has black glass walls with cemented-in quartz windows. The windows must be of quartz to prevent undesirable fluorescence. When not in use, all colloidal material should be thoroughly washed out of the cell to prevent any of it sticking to the windows.

In order to obtain higher intensities of illumination, a number of dark-field condensers have been designed. Prominent among these

[1] SIEDENTOPF and ZSIGMONDY, *Ann. Physik*, (4), **10**, 1 (1903).

are the paraboloid[1] and cardioid[2] dark-field condensers of Siedentopf, and the dark-field condenser of Jentzsch.[3]

The use of the dark-field condensers to which reference has been made is not, however, without disadvantages. With them, it is practically impossible to tell anything about the shape or orientation of the particles, because in these condensers light enters from all sides. In the so-called azimuth diaphragm condenser, designed by Szegvari,[4] light from two diametrically opposite directions only can enter the cell, so that it is possible to change the direction of the light in the cell by simply turning the diaphragm about its axis. Thus, if the particles are not spherical, but elongated, and are oriented in the medium, this fact can be detected with the azimuth diaphragm. It appears to offer many possibilities in the study of the shapes of colloid particles.

The Tyndallmeter.—When a colloidal system is illuminated, light is scattered by the individual particles. This dispersion of light is known as the "Tyndall effect," and the instrument used to measure the effect quantitatively is known as the "tyndallmeter." The Tyndall beam serves for studies of very small particles, particles whose diameter is of the order of magnitude of the wave length of the light used. When the colloidal system contains particles whose size is larger, they must be removed by ultrafiltration or by centrifuging.

In tyndallometry, the formula of Rayleigh is used. It gives the relative intensity of the light scattered, at any angle α, by dilute sols of constant volume concentration, containing very small particles. The equation is

$$\frac{I}{I_0} = K \frac{\nu v^2}{\lambda^4} \sin^2 \alpha$$

where I_0 = the intensity of primary light.
   I = the intensity of Tyndall beam at angle of observation α to primary beam.
   ν = the number of particles deflecting the light.
   v = their volume.
   λ = the wave length of light.

Therefore, tyndallometric studies give valuable information concerning the volume of the particles, provided that their number is known. The number of particles may be obtained by means of absolute ultramicroscopic counts.

[1] SIEDENTOPF, *Z. wiss. Mikrosk.*, **24**, 104 (1907).
[2] SIEDENTOPF, *Verhandl. deut. phys. Gesell.*, **12**, 1 (1910).
[3] JENTZSCH, *Verhandl. deut. phys. Gesell.*, **12**, 975, 992 (1910).
[4] SZEGVARI, *Z. physik. Chem.*, **112**, 277 (1924).

A diagram (Fig. 87) of a common type of tyndallmeter is given below.

For further description of the tyndallmeter and its uses, the references give valuable information.[1,2]

Viscometric Apparatus

Capillary tube, falling sphere, and rotating cylinder viscometers have been described on page 326.

The importance of the viscosity of colloidal solutions has been recognized since the time of Graham. An electroviscous effect has

Lummer - Brodhun
Comparator

Prism

Scale attached
to Nicol Prism

Prisms

Source of Light
split into Two
Beams by Clear
Glass Reflector.

Mirror

Beams of Light

Colloidal
System
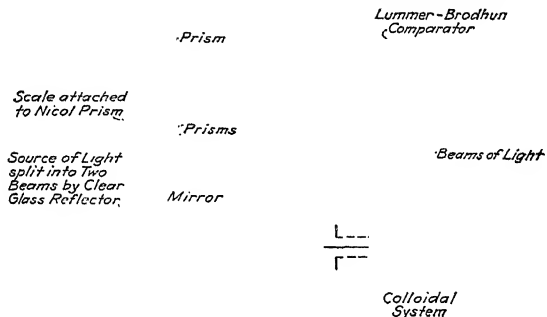
Fig. 87.—Tyndallmeter.

been described by Kruyt.[3] In recent years the theory and practice of the viscometry of dilute solutions of linear polymeric molecules has been considered by Staudinger, Mark, Meyer, Kuhn, Jeffery, Simha, Flory, and others. An excellent summary of these investigations is now available.[4]

In addition to being useful in the determination of viscosity, rotating cylinder viscometers are assembled with optical equipment for the study of the double refraction of flow in solutions containing linear polymers.[5]

[1] FREUNDLICH, "Colloid and Capillary Chemistry," E. P. Dutton & Company, Inc., New York (1922).

[2] WEIGERT, "Optische Methoden der Chemie," Akademische Verlagsgesellschaft, Leipzig (1927).

[3] KRUYT, *Kolloidchem. Beit.*, **28**, 1, 407 (1928); **29**, 396, 413, 432 (1929).

[4] MARK, "Physical Chemistry of High Polymeric Systems," Interscience Publishers, New York (1940).

[5] MEHL, Cold Spring Harbor Quant. Symposia of Biology, VI, 218 (1938); SIGNER, *Trans. Faraday Soc.*, **32**, 296 (1936); SADRON, *J. phys. rad.*, **9**, 381, 384 (1938).

CHAPTER XXII

ELECTRICAL CONDUCTANCE

Electrical Circuits

The general discussion of this section applies to the work in electromotive force as well as to the work in electrical conductivity.

Imperfect connections are the source of considerable trouble in electrochemical experiments. All instruments to be included in an electrical circuit should be provided with binding posts. Wires should not be joined by twisting their ends together, unless they are soldered. It is good practice to cut the wires to the proper length, as this avoids a complicated tangle of wires which is difficult to trace. All mechanical contacts involved in switches and rheostats should be scraped frequently with sand paper and coated with a thin layer of vaseline to make oxide films less troublesome.

A little forethought in planning the arrangement of apparatus will facilitate matters. Before setting up, a rough sketch of connections, with the apparatus in orderly arrangement, should be made. This will assist in checking up and locating possible faults. The connection with the source of current is always made last, after one is assured as to the correctness of the other connections.

A reversing switch may be obtained by simply connecting the diagonally opposite posts of a double-pole double-throw switch with cross wires. When the switch is thrown toward the right, the current in the circuit will flow in one direction; when thrown toward the left, it will flow in the opposite direction.

Keys should be used only in case a very small current is to be carried, otherwise an arc will be produced between the platinum contact points.

Rheostats or variable resistances are usually made with a spring contact sliding along a spiral of resistance wire such as German silver or nichrome. For very small currents the inexpensive type used in radio will do, but for larger currents the horizontal tubular rheostats with two binding posts and a contact sliding along a bar are recommended. The resistance and safe carrying current are marked on the rheostats. Larger currents may be carried if the rheostat is water-cooled. The coil should be kept covered with a thin coating of vaseline

to ensure good electrical contact, and when tarnished the coil and contacts should be cleaned with fine emery paper.

A rheostat, with more certain electrical contact, can be made by dipping an amalgamated mangamin wire into a narrow vertical tube filled with mercury and moving it up or down.

Galvanometers

The d'Arsonval or moving-coil galvanometer is generally used, although the Thomson galvanometer with a light needle moving between fixed magnetic coils is used sometimes when high sensitivity is needed.

The current sensitivity is the current required to give a deflection of 1 mm at a distance of 1 m, and the voltage sensitivity is the voltage that must be applied to the circuit, including both galvanometer and external critical damping resistance, in order to give this standard deflection of 1 mm at a distance of 1 m.

The critical damping resistance is defined as the amount of resistance external to the galvanometer which must be in the circuit to make the galvanometer come back to rest in its zero position in the shortest time after being deflected. If the external resistance is too large, the galvanometer returns very slowly to zero; if it is too small, it oscillates back and forth. It is essential to have the galvanometer critically damped. If the galvanometer cannot be selected for the proposed work or the circuit designed to suit the galvanometer, it may be necessary to add resistance in series with the circuit if it is underdamped or to shunt the galvanometer with a suitable resistance if it is overdamped even though these operations reduce the sensitivity. An ordinary laboratory has use for low-resistance galvanometers (20 to 100 ohms) for thermopile work and calorimetry and for high resistance galvanometers (over 1,000 ohms) for measurements of electromotive force.

Several different models[1] are available depending on sensitivity, ruggedness, and price. The portable-needle type has a current sensitivity of about 10^{-5}, and the portable-box type containing a beam of light reflected on a scale has a sensitivity of about 10^{-7}. For greater sensitivity the galvanometer must be mounted in a stationary position, usually with a screw tripod, and the beam of light from a single-filament lamp is focused on a distant scale with the help of a long-focus lens (1 m) attached to the glass window of the galvanometer.

If a sensitivity much greater than 10^{-8} amp. or 10^{-7} volt is required with a low critical damping resistance, it is necessary to use a special

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[1] "Galvanometers," Leeds & Northrup Company, Philadelphia.

type of galvanometer or some type of amplification. If the current is subjected to mechanical interruption, it can be amplified with vacuum tubes in a radio circuit. An effective method of obtaining very high sensitivity consists in using two galvanometers,[1] the first being connected in the circuit and the second being connected to a thermocouple or a photoelectric cell or photronic cell across which the beam of light from the first galvanometer passes and increases the area exposed. With arrangements of this type the only limit to sensitivity is the natural limit of the irregular motion of the individual electrons due to their Brownian motion.

Special galvanometers are available for alternating current, but they are less sensitive and less satisfactory.

Ammeters and voltmeters are essentially portable galvanometers of low sensitivity. The ammeters for registering current are of very low resistance and are connected in series in the circuit. Voltmeters, for measuring the potential between two points in a circuit, on the other hand, are connected in parallel with the circuit, and their resistance must be so high that only a small fraction of the current flows through them.

Wheatstone Bridge

The principle of operation and the construction of the Wheatstone bridge are indicated on page 177. Alternating current must be used to prevent electrical polarization and the formation of a nonconducting gas film on the electrodes. Accordingly, a telephone is used instead of a sensitive galvanometer which requires direct current. The frequency of the alternating current must then be such that it falls within the audible range, and to be free from all electrolysis the current must be of a pure sine wave, with the current in one direction exactly offsetting that in the other. The resistance coils of the Wheatstone bridge must be wound noninductively, *i.e.*, the wire is doubled back in the middle and the two parts of the wire with current going in opposite directions are side by side. In this way, induction effects are eliminated.

The microphone hummer is an inexpensive and, at the same time, very satisfactory source of alternating current. The frequency is maintained at a constant value by the vibration of an electrically driven tuning fork which actuates the microphone. The magnet that keeps the fork in vibration is supplied from the secondary of a transformer which is operated by the current through the microphone. The wave from this instrument is anything but pure, but if the hummer is

[1] Moss, *J. Sci. Inst.*, **12**, 141 (1935); TAYLOR, *Rev. Sci. Inst.*, **8**, 124 (1937).

remote from the Wheatstone bridge, little difficulty is encountered in determining the balance point.

For accurate work the electron-tube oscillator is now widely used for measuring the electrical conductance of solutions. If properly constructed it gives a pure sine wave current and standard radio equipment may be used. The simplest circuit is shown in Fig. 88.

The grid G and filament F of the vacuum tube, in this particular circuit, are connected to the branched circuit containing inductance L and capacity C, which constitute the oscillatory circuit. The induct-ance and capacity must be of sufficient magnitude to produce an audio-frequency. For this purpose $L = $ about 150 millihenries and $C = 0.7$ μf. The waves generated in this circuit are composed of a fundamental constituent corre-sponding in frequency to that of the waves of current supplied to the circuit due to the passage of electrons from the filament to the plate P and grid. This fundamen-

Fig. 88.—Electron-tube oscillator for measuring the conductance of solutions.

tal constituent may be changed at will, to any desired frequency, by adjustment of the inductance and capacity in the circuit. When desired, the overtones may be removed by suitable filters and chokes.

For satisfactory operation, however, it is necessary to use certain special types of tubes and other equipment. Details for construction of an inexpensive apparatus for laboratory use are given by Roseveare and Goff.[1]

In adjusting the Wheatstone bridge, it may not be possible to find a position on the dials which will give dead silence. In such a case the mean position is taken between two positions of equal sound intensity. The capacity as well as the resistance affects the setting of a Wheat-stone bridge, and in accurate work it is desirable to have a variable condenser shunted around the conductance cell so that it may be brought to the position that will give the minimum of sound when the final adjustment is made.

For work of the highest precision many precautions must be observed and special apparatus designed.[2-4]

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[1] ROSEVEARE and GOFF, Forthcoming publication.

[2] JONES and JOSEPHS, *J. Am. Chem. Soc.*, **50**, 1049 (1928).

[3] SHEDLOVSKY, *J. Am. Chem. Soc.*, **52**, 1793 (1930).

[4] LUDER, *J. Am. Chem. Soc.*, **62**, 89 (1940).

Conductance Cells

A simple form of conductance cell was shown on page 177. Two platinum plate electrodes are welded or gold-soldered to stout platinum wires and sealed into soft glass with lead glass. The external leads of copper wire are welded to the platinum wires, or they are connected with a drop of mercury. The simplest type of cell to construct uses platinum wires with the ends spiralled into flat pancake coils taking the place of platinum foil. For solutions of low conductance the electrodes

should be large and close together. For solutions of high conductance they should be smaller and farther apart. A cell should be constructed so that it can be immersed in the water of a thermostat and so that it can be readily filled, emptied, and rinsed. Cracks or close edges difficult to rinse must be avoided.

The cell shown in Fig. 89 was designed by Jones and Bollinger[1] after a thorough investigation. In it the electrode leads are far apart,
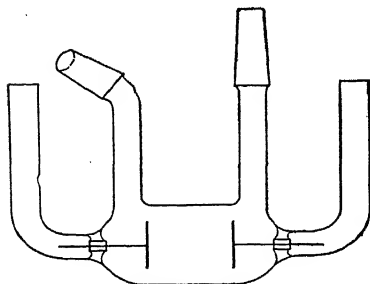
FIG. 89.—Conductance cell for solutions.

thus minimizing the danger of capacity changes with their apparent effect on variations in the cell constant.

The capacity of the cell and bridge arms may introduce an error if not eliminated, particularly when the frequency is high or the capacity is great. There may be an error from self-induction in the bridge coils, if they are not properly wound, which is larger with high frequency and small resistance. Polarization is most serious when the frequency and the resistances are low.

Polarization may be practically eliminated by using an alternating current pure sine wave of moderate frequency, and by coating the electrodes with platinum black. The electrodes can be platinized by immersing them in a solution containing 3 g of platinic chloride and 0.02 g of lead acetate in 100 ml of water, and connecting them to two dry cells connected in series. The current is regulated by means of a rheostat so that only a small amount of gas is evolved. After the electrodes are coated with platinum black, they are removed from the solution and thoroughly washed with distilled water. Any traces of chlorine adsorbed from the plating solution may be removed by con-

[1] JONES and BOLLINGER, *J. Am. Chem. Soc.*, **53**, 411 (1931).

tinuing the electrolysis, with the same connections, in a dilute solution of sulfuric acid.

For work in very dilute solutions, which has become of great theoretical importance, the platinized surface must be dispensed with because it is so difficult to rinse out the last traces of electrolyte from it. Bright platinum electrodes are used, and special precautions are followed to ensure a pure sine-wave current.

Conductance of Potassium Chloride Solutions.—In a very careful and exacting research, Jones and Bradshaw[1] have redetermined the electrical conductance of standard potassium chloride solutions for use in the calibration of conductance cells. The results of the work are summarized in the table that follows.

SPECIFIC CONDUCTANCE OF STANDARD POTASSIUM CHLORIDE SOLUTIONS IN OHMS^{-1} CM^{-1}

Grams of potassium chloride per 1,000 g of solution in vacuum	Specific conductance		
	0°C.	18°C.	25°C.
71.1352	0.065176	0.097838	0.11342
7.41913	0.0071379*	0.0111667	0.0128560
0.745263	0.00077364	0.00122052	0.00140877

* The lowering of the last figure indicates that this figure is uncertain.

Conductance Water

In all conductance measurements made in aqueous solution it is necessary to have very pure water. Distillation in a seasoned glass vessel and condenser with ground-glass joints or with a block tin condenser can give water with a specific conductance of about 1×10^{-6} reciprocal ohm if a little potassium permanganate is added to the flask. In such a distillation carried out in air the water is saturated with the carbon dioxide of the air (0.04 per cent). Some of the dissolved carbon dioxide can be removed to give a higher resistance by bubbling through carbon dioxide-free air.

It is interesting to note that Kohlrausch and Heydweiller[2] reported the preparation of purified water with a specific conductance at 18° of only 0.043×10^{-6} reciprocal ohm.

Conductance water for laboratory use may be prepared on a large scale by distilling distilled water and condensing in a block tin con-

[1] JONES and BRADSHAW, *J. Am. Chem. Soc.*, **55**, 1780 (1933).
[2] KOHLRAUSCH and HOLBORN, "Leitvermögen der Elektrolyte," 2d ed., B. G. Teubner, Leipzig (1916).

denser while a current of purified air is sweeping through the condenser in the opposite direction.   The air is bubbled through sodium hydroxide solution and then through a solution of potassium permanganate and sulfuric acid.

The subject of conductance in nonaqueous solutions has been developed by Kraus and his associates.[1]

[1] KRAUS, "The Properties of Electrically Conducting Systems," Reinhold Publishing Corporation, New York (1922).

CHAPTER XXIII

ELECTROMOTIVE FORCE

Potentiometer

The principle of the potentiometer is shown in Fig. 90 in which the electromotive forces or potentials of two batteries A and B may be compared. A wire RS, of uniform resistance, is stretched along an ordinary meter stick. The current is supplied by battery B, whose electromotive force is larger than that of battery A. Since the wire is of uniform resistance and the same current passes through each section of it, there will be a uniform fall of potential per unit length in the direction R to S. To measure an unknown electromotive force (battery A), a second circuit containing a key, galvanometer, and sliding contact is necessary. The positive of battery A is connected
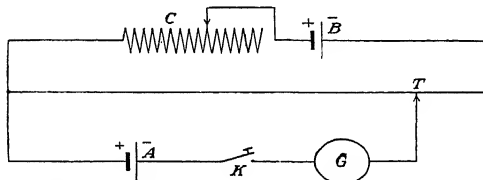
FIG. 90.—Principle of the potentiometer.

opposite the positive of battery B, at R. The sliding contact T is moved along the wire, until there is no deflection of the galvanometer G when the key K is pressed. If the sliding key is moved too far to the right, the galvanometer will deflect in one direction; if too far to the left, the galvanometer will deflect in the other direction. If the potential drop per unit length of the slide wire is known, the electromotive force of the battery A may be determined directly from the length RT; or, knowing the electromotive force of battery B (and eliminating the rheostat C shown in Fig. 90), that of battery A may be determined by the relation

$$\frac{\text{E.m.f. of } A}{\text{E.m.f. of } B} = \frac{\text{length } RT}{\text{length } RS}$$

The potentiometers manufactured for laboratory use are designed so that the fall of potential per unit length of wire can be adjusted to

some decimal fraction of a volt, and the unknown voltage can be read directly from a scale. This is accomplished by means of the control rheostat C, using a Weston cell, in place of battery A. The Weston standard cell has a voltage of 1.0183. The point T is adjusted to space 1018.3 divisions of the wire RS. The current through the wire is then adjusted by the control resistance C, until the galvanometer shows no deflection, which means that the fall of potential along RT is 1.0183 volts, and the fall of potential per unit length is 1 millivolt. Having once adjusted the potentiometer with the rheostat C against the standard cell, the readings thereafter are given directly in voltages.

Standard Cells

Of the various types of standard cells which have been proposed from time to time, the Weston or cadmium standard cell, shown in
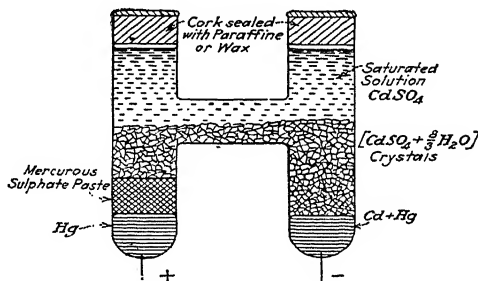
FIG. 91.—Weston cadmium standard cell.

Fig. 91, is the one now most generally employed.[1] This cell is set up in an airtight, H-shaped vessel, with platinum wires sealed through the bottoms for connection with the electrodes. The positive electrode consists of pure mercury, which is protected by a covering of a thick paste of mercurous sulfate and a small quantity of cadmium sulfate. The negative electrode is a cadmium amalgam containing 12.5 per cent of cadmium. On the top of the solidified amalgam and of the mercurous sulfate paste are placed some rather large and clear cadmium sulfate crystals; then the cell is filled with a saturated solution of cadmium sulfate. The ends of the tubes are closed, allowing sufficient air space for thermal expansion. The materials must be thoroughly purified.

[1] VOSBURGH, *J. Am. Chem. Soc.*, **47**, 1255 (1925); VOSBURGH and DERR, *J. Chem. Ed.*, **18**, 87 (1941).

The electromotive force of this cell, in terms of the international ohm and ampere, is

$$E = 1.0183 \pm 0.0001 \text{ volts at } 20°C.$$

The temperature coefficient of the cell is small, it being given with accuracy sufficient for most purposes by the expression

$$E_t = E_{20} - 0.0000406(t - 20)$$

Standard Electrodes

The cells whose electromotive forces are to be determined may be considered to be made up of two electrodes, one an indicator electrode and the other a reference electrode. The most convenient reference electrode is the calomel electrode, one form of which is shown in Fig. 40, page 189.

There are three types of calomel electrodes in common use, depending upon the concentration of the potassium chloride solution used: tenth-normal, normal, and saturated. In the work described in this book the normal calomel electrode is used. The calomel electrode is prepared as follows: The glass vessels are cleaned and rinsed thoroughly, using distilled water for the latter operation. The sealed-in platinum wire, fused to a copper wire, is in contact with specially purified mercury. The calomel paste is made by grinding calomel in a mortar with purified mercury and potassium chloride solution of the concentrations indicated above (depending on the type of electrode to be used). It is placed above the mercury to a depth of approximately 1 cm. The tube and the bridge are then filled with potassium chloride solution of the desired concentration. The end of the bridge is stoppered with a ground-glass plug, the current being carried by the thin liquid film between the wall of the tube and the plug. It is preferable to have the tube made of pyrex and the plug of soft glass. If the plug is cooled before insertion into the tube, it will become firmly fixed upon subsequent heating to room temperature. This type of junction has a high resistance and requires the use of a high-resistance galvanometer (approximately 1,000 ohms) in the potentiometer circuit. A junction of this type should be kept immersed in potassium chloride solution when not in use so that the liquid film will not dry out. An alternative method of reducing diffusion at the junction involves constricting the end of the bridge arm to a tip, which contains solidified agar. This connecting bridge has a much lower resistance than the type with a ground-glass joint. Better still is a simple connecting salt bridge with sintered glass at the ends.[1]

[1] LAITINEN, *Ind. Eng. Chem. Anal. Ed.*, **13**, 393 (1941).

The silver chloride electrode is perhaps next in importance to the calomel cell as a reference half-cell. It is reversible, with respect to both silver and chloride ions, and it can be inserted directly into a solution in an electrochemical cell without introducing a liquid junction. It is made by depositing silver electrolytically on a coil of platinum wire which is fused to a copper lead and then sealed into a glass tube. This silver electrode is then made the anode in a solution containing a chloride, and a coating of silver chloride is deposited directly on the silver. A standard form is shown in Fig. 92.

The preparation of a mercury-mercurous sulfate electrode is similar to that of the calomel electrode. Pure mercury and pure mercurous

Platinum Wire

Colloidal Ag+AgCl
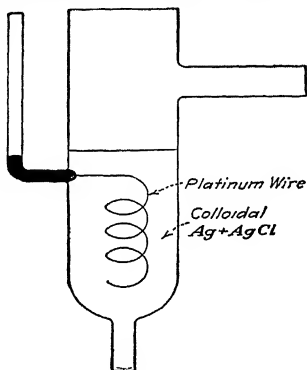
Fig. 92.—Silver chloride electrode.

sulfate are shaken several times with the sulfuric acid solution with which the electrode is to be used. After each shaking, the liquid is decanted off. Mercury in the reservoir of the electrode vessel is covered with a paste formed by grinding the mercurous sulfate and a little mercury, while they are still moist, with the sulfuric acid. In the electrode proper the platinum wire should not be allowed to come into contact with the acid; therefore, it is convenient to seal the wire through the glass bottom of the reservoir.

The preparation and purification of mercurous sulfate for use in the electrode have been described by Hulett.[1] Mercury-mercurous sulfate electrodes have been used with success by Brönsted,[2] Randall and Cushman,[3] and by others.

[1] HULETT, *Phys. Rev.*, **32**, 257 (1911).
[2] BRÖNSTED, *Z. physik. Chem.*, **68**, 693 (1910).
[3] RANDALL and CUSHMAN, *J. Am. Chem. Soc.*, **40**, 393 (1918).

In the following table are collected data for the more common reference electrodes, the potentials being referred to the normal hydrogen electrode.

REFERENCE-ELECTRODE POTENTIALS AT 25°C.

Reference electrode	Concentration, moles per liter	Potential
$H_2\|H^+(a = 1)$...................		0.000
$Hg\|Hg_2Cl_2$, KCl...............	1.0	+0.2805
	0.1	+0.336
	3.5 sat.	+0.246
$Hg\|Hg_2Cl_2$, HCl...............	0.1	+0.335
$Ag\|AgCl$, KCl.................	0.1	+0.290[1]
$H_2\|HCl$.......................	0.1	−0.064
$H_2\|\frac{1}{2}H_2SO_4$...................	0.1	−0.073
$Hg\|Hg_2SO_4$, $\frac{1}{2}H_2SO_4$...........	0.1	+0.682
$H_2\|NaOH$......................	0.1	−0.761
$Hg\|HgO$, NaOH...............	0.1	+0.165

[1] HARNED and EHLERS, *J. Am. Chem. Soc.*, **55**, 2179 (1933).

CHAPTER XXIV

ELECTRODE PHENOMENA

Coulometers

The most accurate of all coulometers is the silver coulometer. Moreover, it is commonly accepted as the standard, since the definition of the coulomb depends on the amount of silver electrolyzed from silver nitrate solution under well-defined conditions.

The silver coulometer has been the subject[1,2] of considerable study. It is shown diagrammatically in Fig. 93.[3] The electrolyte is a 15 per cent solution of pure silver nitrate. When 3 g of silver has been deposited from 100 ml of the solution, the electrolyte must be renewed. The current density at the anode should not be greater than 0.2 amp. and at the cathode not greater than 0.02 amp. per square centimeter
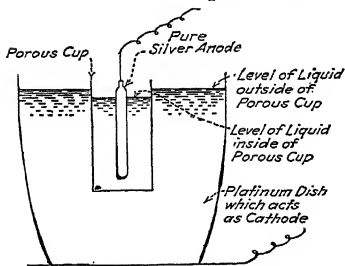
Special precautions are necessary for weighing the platinum cathode. It should be thoroughly washed with distilled water (*i.e.*, until the wash water gives no test for silver with hydrochloric acid). It is then thoroughly washed with distilled water at 70 to 90°, after which it is dried in an electric oven at about 150°C. and, after at least 10 min. in a desiccator at room temperature, it is weighed.

FIG. 93.—Silver coulometer.

The copper coulometer, although not at all the precision instrument that the silver coulometer is, finds frequent use in practical laboratory operations. It consists preferably of two copper anodes and a pure copper cathode between the anodes, in a solution of copper sulfate to which an excess of sulfuric acid has been added. A suitable electrolyte

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[1] RICHARDS, COLLINS, and HEIMROD, *Z. physik. Chem.*, **32**, 336 (1900); WASHBURN and BATES, *J. Am. Chem. Soc.*, **34**, 1341 (1912); BATES and VINAL, *ibid.*, **36**, 916 (1914); ROSA, VINAL, and MacDANIEL, *Bur. Standards Bull.*, **10**, 475 (1914).

[2] BOVARD and HULETT, *J. Am. Chem. Soc.*, **39**, 1077 (1917).

[3] Filter-paper wrapping may be substituted for the porous cup in all except precision measurements. Filter paper has a slight reducing action which makes the silver deposits too heavy.

contains 150 g copper sulfate, 50 g sulfuric acid, and 50 g of alcohol, dissolved in 1,000 ml of distilled water. The cathode current density should be between 0.002 and 0.02 amp. per square centimeter. This coulometer has been described in a number of places in the literature.[1-3]

Second only in accuracy to the silver coulometer is the so-called iodine coulometer, in which the iodine liberated from a potassium iodide solution at the electrode is titrated with a standard sodium thiosulfate solution. The original iodine coulometers utilized a potassium iodide solution which had been acidified with hydrochloric acid.[4] In more recent years, Washburn and Bates[5] and Bates and Vinal,[6] using a neutral solution of potassium iodide, have established the iodine coulometer as an instrument of precision (page 236).

Titration coulometers are extremely useful in cases where small amounts of current are to be measured, since they avoid the errors inherent in the weighing of an electrode where very small differences in weight are expected.

Volume coulometers are used only in the measurement of comparatively large quantities of electricity. In this classification are found the water coulometer and the mercury coulometer.

The water coulometer consists of a glass vessel, into which two platinum electrodes are sealed, connected to a gas burette. The electrolyte is a 15 per cent sodium hydroxide solution. As the current passes from one electrode to the other, water is decomposed, forming oxygen and hydrogen in the ratio of volumes given by the equation

$$H_2O \rightarrow H_2 + \tfrac{1}{2} O_2$$
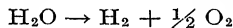
The number of cubic centimeters of gas evolved, as measured on the burette, determines the amount of electricity which has passed. A correction is made for the vapor pressure of water.

The mercury coulometer is one from which mercury is separated from the electrolyte—a solution of the iodides of potassium and mercury—and is allowed to fall into a graduated tube. It is a commercial rather than scientific instrument.

Rectifiers

The most common laboratory method of rectifying an alternating current is probably by means of the "Elkon" or "Kuprox" type

[1] FOERSTER, *Z. anorg. Chem.*, **14**, 106 (1897); *Z. Elektrochem.*, **3**, 493 (1897).

[2] RICHARDS, COLLINS, and HEIMROD, *Z. physik. Chem.*, **32**, 321 (1900).

[3] DEDE, *Z. Elektrochem.*, **17**, 238 (1911).

[4] DANNEEL, *Z. Elektrochem.*, **4**, 154 (1897); KREIDER, *Physik. Z.*, **6**, 582 (1905).

[5] WASHBURN and BATES, *J. Am. Chem. Soc.*, **34**, 1341 (1912).

[6] BATES and VINAL, *ibid.*, **36**, 916 (1914).

metal–metal oxide instrument. These units are small, cheap and readily portable. The principle upon which these rectifiers operate is suggested by Slepian.[1] They are excellent for use in situations where the drain on ordinary dry batteries would be too high for economy.

The use of vacuum tubes for rectification purposes is also widespread. Many practical units for operating relays and other electromagnetic devices of the physical-chemical laboratory are available. A typical example of this type of instrument is the power pack in present-day radio sets. The function of the vacuum tube in rectification is indicated on page 431.

For central-service operation a motor-generator set provides a satisfactory installation. The motor is operated on alternating current, whereas the generator which is coupled to it produces direct current. Outlets are wired through a switchboard to laboratory desks.

There are other types of rectifier that are sometimes used. Tungar (gas-discharge) assemblies are useful for charging portable storage batteries, but replacement tubes for them are now difficult to obtain. Another type depends on the fact that metals such as aluminum, antimony, bismuth, and tantalum in alkali solution, when acting as electrodes, exert a "valve" action in which they allow the current to flow only in the direction for which they are the cathode. Lead or platinum is generally used as the second electrode in the cell. The simple metal–metal oxide rectifier has practically replaced the liquid-cell type.

[1] SLEPIAN, *Trans. Am. Electrochem. Soc.*, **54**, 201 (1928).

CAPACITY

Farad Bridges.—The farad bridge is similar in all respects to the Wheatstone bridge, except that two (or four) of the resistances of the latter are replaced by capacities.

If the condenser being investigated has a liquid dielectric medium with appreciable electrical conductance, special forms of bridge must be utilized to measure its capacity. The most commonly used bridge is some form of that described by Nernst,[1] in which the conductance on one side of the bridge is compensated by another conductance on the other side.

Radio-frequency Bridge.—It is a difficult problem to determine the position of balance with a bridge when using alternating current at high frequencies. Bridge circuits present many difficulties peculiar to high-frequency work, such as stray capacity effects between parts of the bridge and between operator and source of oscillations. In spite of the fact that some authorities suggest breaking away from the methods that have proven so successful at the lower frequencies, several excellent bridge systems have been developed especially for high-frequency work.

A high-frequency bridge now in successful use (shown in Fig. 94) uses an electron-coupled oscillator as power source. The screen-grid detector-generator circuit acts both as weak oscillator and as null-point indicator. This weak oscillator heterodynes its frequency with that of the electron-coupled power oscillator to give an audio-frequency beat note. The audible beat note, rectified by the screen-grid tube, is used for the null indication. For the reception of the signals, the use of an audio-amplifier is recommended. It is a very satisfactory bridge, making possible capacity and dielectric-constant determinations with liquids having an appreciable conductance.

Resonance Method for Capacity.—For work at the higher frequencies, the resonance methods have many advantages. In principle, a circuit called the "resonator," containing the unknown capacity, is

[1] NERNST, *Z. physik. Chem.*, **14**, 622 (1894); TURNER, *ibid.*, **35**, 385 (1900); TANGL, *Ann. Physik*, **23**, 559 (1907); SACK, *Physik. Z.*, **28**, 199 (1927); SKANCKE and SCHREINER, *Physik. Z.*, **28**, 597 (1927).

brought, by the adjustment of a variable condenser, to resonance with an oscillator that is maintained at a fixed frequency.   This condenser, after calibration, is connected in parallel with the dielectric cell, and capacity measurements are made in the manner described on page 253. This method is satisfactory at high frequencies only if stray-capacity effects in the resonator can be eliminated.

Radio Frequency
Bridge

Screen-Grid
Detector – Oscillator
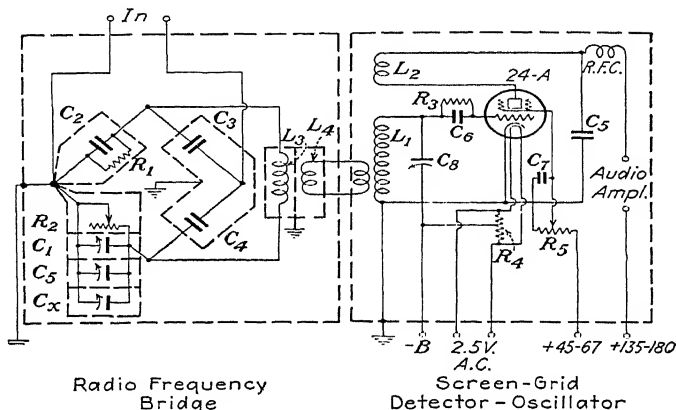
FIG. 94.—Capacity bridge for measurement at radio frequencies.

C_1 = 1500-$\mu\mu$f variable air condenser.
C_4 = 1500-$\mu\mu$f variable precision condenser.
C_x = dielectric cell.
C_2, C_3, C_4 = 2000-$\mu\mu$f fixed mica condenser.
C_5, C_6 = 250-$\mu\mu$f fixed mica condenser.
C_7 = 0.5-μf fixed mica condenser.
C_8 = 250-$\mu\mu$f variable air condenser.
R_1 = 500- to 2000-ohm fixed noninductive resistance.
R_2 = 10,000-ohm variable noninductive noncapacitative resistance.
R_3 = 2-megohm grid leak.

R_4 = 50-ohm center-tapped resistor.
R_5 = 100,000-ohm potentiometer.
L_1 = inductance.   Number of turns dependent upon frequency used in bridge.
L_2 = inductance.   One-sixth of L_1 and wound on same coil form.
L_3, L_4 = inductances wound on 1-in. coil form.   The inductance L_1 completes coupling of bridge with detector-oscillator.
In = input from power oscillator.
R.F.C. = radio-frequency choke.
Dotted lines indicate metal shields.

For precision determinations it is desirable to use a very sensitive vacuum-tube detector circuit.   In one such detector,[1] shown in Fig. 95, an a-c voltage across points D and E will indirectly cut off the main plate current in the vacuum tube.   The power from the standard oscillator is adjusted so that the plate current at the resonance point is only a few microamperes.   This detector is very sensitive to changes in the a-c voltage across the cell.   A 1.5-volt dry cell is inserted in such a manner that the minimum in the plate current at the resonance point is changed into a maximum.   This circuit was designed for use with a

[1] ELLIOTT and WILLIAMS, *J. Am. Chem. Soc.*, **61**, 718 (1939).

twin-capacity cell for solvent and solution in the study of the frequency variation of the dielectric constant of protein solutions.

Wyman[1] has described a modification of the resonance method which avoids some of the difficulties of the ordinary method at high frequencies. Small rigid resonators are constructed, which can be entirely immersed in the liquid to be studied, and in this way all the capacities of the circuit are included within the medium. In operation, the method is an inversion of the usual procedure of tuning the resona-
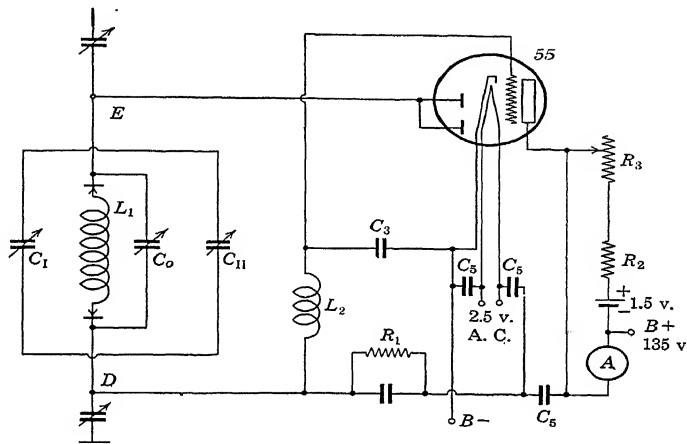
FIG. 95.—Resonance detector circuit.

C_1 = solution cell.	R_1 = 500,000-ohm fixed resistor.
C_{11} = solvent cell.	R_2 = 100-ohm fixed resistor.
C_0 = midget variable condenser.	R_3 = 40,000-ohm variable resistor.
C_3 = 500-$\mu\mu$f fixed mica condenser.	L_1 = inductance.
C_4 = 250-$\mu\mu$f fixed mica condenser.	A = multimeter.
C_5 = 0.01-μf fixed mica condensers.	L_2 = radio-frequency choke.

tor to the oscillator, because in making a measurement the frequency of the oscillator is varied until it corresponds with the natural period of the resonator, first in air and then in the liquid. These two frequencies are necessary for the calculation of the dielectric constant; therefore they must be determined with a considerable degree of accuracy. This may be accomplished by heterodyning the unknown frequencies with those of quartz-crystal-controlled oscillators, using either the fundamentals or harmonics of the latter. Further details are available in the original article.

[1] WYMAN, *Phys. Rev.*, **35**, 623 (1930).

A recent book by Hartshorn[1] gives much valuable information about measurements at radio-frequencies.

Heterodyne-beat Method for Capacity.—For dielectric-constant measurements with liquids of very low conductance, such as solutions of polar molecules in benzene, the heterodyne-beat method is recommended because of its extremely high accuracy, and because it is a very sensitive procedure for measuring very small high-frequency capacities. It makes use of two oscillators, with one detector-amplifier circuit. It depends on the interaction of the frequencies of the two oscillators to give a point of silence in the audio receiver when their natural periods become alike. The two oscillators and the detector amplifier are contained in separate metal boxes for shielding, the coupling of the circuits being made through holes drilled in the shields. Two forms of heterodyne-beat apparatus are described in Exp. 63. In one of these assemblies a radio broadcasting station is used as a standard source of oscillations.

Fig. 96.—Electron-coupled oscillator.

C_1 = 500-$\mu\mu$f variable air condenser.
C_2 = 250-$\mu\mu$f fixed mica condenser.
C_3 = 40-$\mu\mu$f fixed mica condenser.
C_4 = 0.01-μf fixed mica condenser.
R_1 = 50,000-ohm fixed resistor.
R_2 = 50,000-ohm fixed non-inductive resistor (2 watt).
L_1 = inductance wound for desired frequency.
Dotted line indicates metal shield.

In cases where extreme accuracy in a capacity measurement is required, an audio frequency may be employed to assist the determination of the end point. A convenient source of this third frequency is a microphone hummer giving 1,000 vibrations per second. The frequency of the measuring-circuit oscillator is then adjusted until it gives 1,000 beats per second with the standard oscillator, i.e., until there is no difference in frequency between the beat note and the microphone hummer. This adjustment will be more exact than one made to zero beat note between the oscillators, because with the interaction of the two frequencies there is a tendency to interlock at and near the equivalence point, giving a small space of silence rather than a point of silence.

Electron-coupled Oscillator.—A new type of oscillator[2] has been developed which has many advantages for dielectric-constant work.

[1] Hartshorn, "Radio-Frequency Measurements by Bridge and Resonance Methods," John Wiley & Sons, Inc. (1941).
[2] Dow, *Proc. Inst. Rad. Eng.*, **19**, 2095 (1931).

It is stable and it is very rich in harmonics, making it convenient for use in the study of the variation of dielectric constant with frequency. The electron-coupled oscillator is a variation of the regenerative triode oscillator, in which the screen of a tetrode takes the circuit position ordinarily occupied by the triode plate and radio frequency can be taken from the plate circuit.

There is shown in Fig. 96 an electron-coupled oscillator which has been used with the high-frequency bridge described above.

Modified Ultraudion Oscillator.—In the experiments that describe the measurements of dielectric constant, using the resonance and heterodyne-beat methods, high-frequency vacuum-tube oscillators of the Hartley type are described. Other types of oscillators may also give very satisfactory results. The circuit diagram for one such source which has much to recommend it, especially for work with the resonance method, is shown in Fig. 97. A particular advantage of this form of oscillator is the isolation of the high-frequency current in the grid-plate circuit, making it less sensitive to stray-capacity effects, and, therefore, more stable in operation. It may

Fig. 97.—Modified ultraudion oscillator.

be used at very high frequencies. A No. 45 vacuum tube with a "midget" power transformer makes an effective combination.

Other Oscillators.—New types of oscillators are continually being developed. Two which have much better frequency stability than the Hartley circuits are the dynatron oscillator of Groszkowski[1] and the transitron oscillator of Brunetti.[2]

Dielectric Cells.—There are many factors that determine the choice of type of dielectric cell to be used in any given experiment. Low-capacity cells are usually desired for work with aqueous solutions. An assembly that gives adequate shielding, rapid heat exchange with water circulated about the container from the thermostat bath, low capacitative and inductive effects between leads, and exactness in
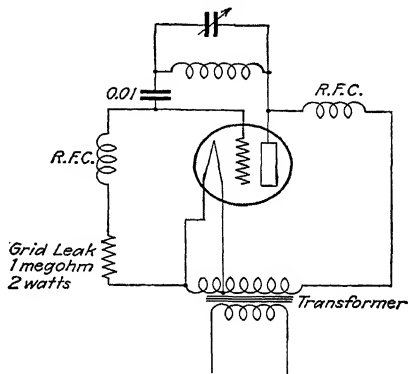
[1], *Proc. I.R.E.*, **22**, 145 (1934).
[2] BRUNETTI, *Proc. I.R.E.*, **27**, 88 (1939).

operation has been described by Albright.[1] This cell proper is shown in Fig. 98.

For work with a sensitive resonance apparatus at high frequencies, Elliott and Williams[2] have devised a twin-capacity cell for solvent and solution to minimize errors due to inductance effects at such fre-
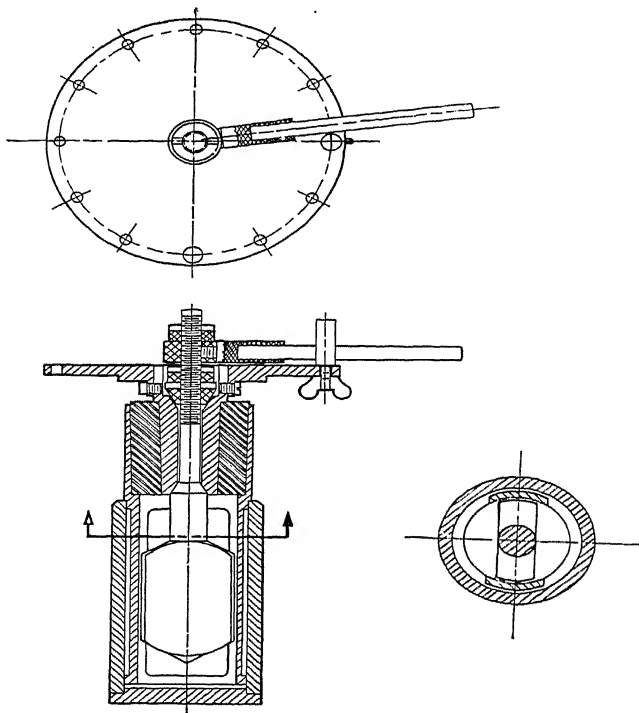
FIG. 98.—Dielectric cell.

quencies. This system resonates readily at 20 to 30 megacycles with aqueous solutions and at 50 megacycles with dilute benzene systems. The construction of the twin cell is suggested by Fig. 99. Each container holds 25 ml, and each condenser is of the midget variable type with all but three plates removed.

[1] ALBRIGHT, *J. Am. Chem. Soc.*, **59**, 2098 (1937).
[2] ELLIOTT and WILLIAMS, *J. Am. Chem. Soc.*, **61**, 718 (1939).

Another type of dielectric cell for use in a radio-frequency bridge and constructed of two platinum cups mounted in a plastic head has been described by Ferry and Oncley.[1] It has small fluid capacity, small electrical capacity (thereby diminishing inductance effects in the bridge), and excellent shielding.

Oscillograph.—The cathode-ray oscillograph is an important instrument for studying the wave form of an oscillator, for measuring the
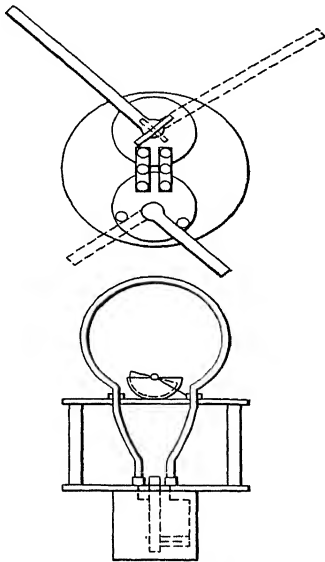
Fig. 99.—Twin cell for measuring dielectric constants.

frequency and peak voltage of the oncoming wave, and for testing radio circuits and public-address systems. In simplest terms it is an electron gun which projects a stream of electrons along the length of a tube, at the end of which is placed a fluorescent screen. The electron beam passes between a horizontal and a vertical set of plates on the path to the screen, so that it may be deflected by voltages applied to the plates. The deflection of the beam is proportional to the voltage applied across the plates; thus the beam acts as the pointer on a voltmeter. The common oscillographs have electrostatic deflection for both horizontal and vertical plates.

[1] Ferry and Oncley, *J. Am. Chem. Soc.*, **63**, 272 (1941).

Throughout most of the applications of the oscillograph both sets of deflecting plates are used to give a two-dimensional diagram on the fluorescent screen so that not only the peak voltage value of a wave but also its value at all points of the cycle is shown.   Both sets of plates are also used to show the relationship existing between two voltages or two currents, or between a voltage and a current.   The Lissajous' figures obtained in this way are used extensively for the comparison of an unknown frequency with a known one for frequency calibration.

The oscillograph is finding applications in physical chemistry. For example, the oscillograph has been proved to be superior to the telephone in determining the conductance of a solution.[1]   The apparatus includes stock instruments, a beat-frequency oscillator, a conductance bridge, a three-tube amplifier, a variable capacitance, and a variable inductance.   When the bridge is perfectly balanced the screen of the cathode-ray oscillograph shows a horizontal straight line. Ellipses are formed when the bridge is not balanced with respect to both resistance and capacity.   Again, the circuit can be arranged to give a sine-wave line when the bridge is unbalanced.

[1] JONES, MYSELS, and JUDA, "The Measurements of the Conductance of Electrolytes. IX.   The Use of the Cathode-Ray Oscillograph as a Detector." *J. Am. Chem. Soc.*, **62**, 2919 (1940).

CHAPTER XXVI

ISOTOPES

Measurements of Radioactivity

When charged electrodes are placed in an ionized gas, the magnitude of the current flowing is a measure of the number of ions reaching the electrodes. When the voltage is so high that an increase in voltage produces no further increase in the current, all the ions are being drawn to the electrodes before recombination can occur. The saturation current thus produced is a measure of the total number of ions, which in turn is a measure of the radioactivity. The ionization current is measured conveniently with an electroscope or electrometer.

Electroscopes.—The electroscope measures electrostatic leakage by measuring the rate of fall for a strip of very fine gold leaf or aluminum foil. A leaf hangs by the side of a central metal rod, which is well insulated from the ground, preferably with a bushing of amber. When a charge is applied to this rod, the leaf, in electrical contact with it, acquires the same charge and is repelled. The electroscope may be charged with about 500 volts from radio B batteries, a dynamo, or a hard rubber stick which has been charged by rubbing on woolen cloth. The charged rod is moved along a connecting wire, which is then touched momentarily to the rod, and the process is repeated until the leaf is repelled to the desired distance.

The edge of the leaf is viewed with a short-focus lens (or telescope), and as it falls the number of divisions of the scale passed over per minute is noted. There is usually a natural leakage due to natural ionization, or to a film of moisture on the surface of the insulator, and a correction must be applied. The natural rate of fall is subtracted from the observed rate.

Electrometers.—The electrometer has a vane which is repelled or attracted by an electrostatic field, and as it rotates it turns a small mirror and deflects a beam of light along a scale. In the quadrant electrometer, which is the most common type, the vane is set between four quadrants which are connected to the circuit. The first and third quadrants of the circle are connected to one electrode of the circuit and the second and fourth to the other electrode. Frequently, one set of

quadrants is connected to the ground. The light metallic vane is suspended by a fine quartz fiber which has been sputtered with platinum or gold to make connection with a set of batteries so that the vane can be charged. The rotation of the vane, as measured by the scale deflection of the beam of light, is proportional to the difference in charge on the quadrants of the electrometer. For high sensitivity it is necessary to keep the capacity of the system as small as possible. If the electrometer is connected across a high resistance in an electrical circuit, the rate of leakage is a measure of the current flowing.[1]

In the hands of Millikan and Cameron[2] the electrometer has been successfully used to measure ionization caused by cosmic radiation, amounting to only 5 ions per second per cubic centimeter.

Geiger–Mueller Counters.—Counting chambers of great sensitivity[3] have been developed for detecting and measuring weak radiations particularly in the study of cosmic radiations and tracer reactions making use of artificially radioactive elements.

An easily ionizable gas is placed between two electrodes charged with a battery just below the sparking potential. When an ionizing radiation enters and produces an ion, a breakdown occurs, a small spark is formed sufficient to let pass a feeble current which is then amplified with a vacuum-tube circuit. An electromagnetic counter which can be purchased from apparatus supply houses is convenient for recording the number of impulses, which is equal to the number of radiations passing into the chamber. They are best adapted to count beta rays which are sufficiently penetrating to pass through the thin glass containing the gas under reduced pressure and because they are largely stopped by the enclosed gas. Larger vessels can be used for gamma rays, and by surrounding the tube with cadmium these instruments may be used for counting neutrons.[4]

The construction and operation of a Geiger–Mueller chamber and circuit is shown diagramatically in Fig. 100. The chamber itself may be purchased or it may be constructed with a central wire through a glass tube silvered or sputtered with metal on the inside and filled with hydrogen at a pressure of a few millimeters.[5] The impulses of current

[1] A full discussion of electrometers and electroscopes with details of construction is given in Strong's "Procedures in Experimental Physics," Chap. VI, Prentice-Hall, Inc., New York (1939).

[2] MILLIKAN and CAMERON, *Phys. Rev.*, **31**, 163 (1928).

[3] GEIGER and MUELLER, *Phys. Zeit.*, **29**, 839 (1928).

[4] A full discussion of these counters and circuits together with details of construction is given by Strong, "Procedures in Experimental Physics," Chap. VII, Prentice-Hall, Inc., New York (1939).

[5] BREWER and BRAMLEY, *J. Applied Phys.*, **9**, 778 (1938).

are amplified and, operating through a thyratron tube, actuate an electromagnetic device which turns counting wheels.

Simple types of counters have been described, and it is possible though unsatisfactory to use a telephone and record the clicks with a pencil or hand counter, thus dispensing with the counting circuit.
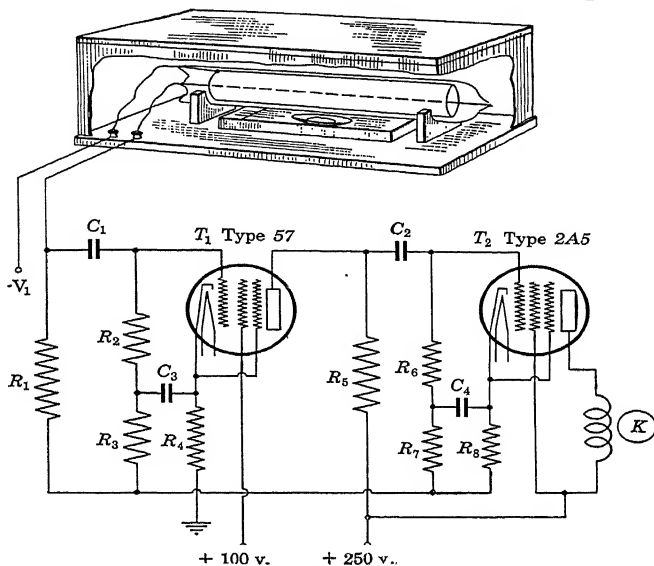
FIG. 100.—Geiger-Mueller counter and circuit.

C_1 = 25 to 50 $\mu\mu$f.
C_2 = 10^{-3} μf.
C_3 = C_4 = 0.1 μf.
R_1 = 1 to 5 × 10^9 ohms.
R_2 = 5 × 10^6 ohms.
R_3 = 0.5 × 10^6 ohms.

R_4 = 3000 ohms.
R_5 = R_7 = 0.1 × 10^6 ohms.
R_6 = 0.2 × 10^6 ohms.
R_8 = 2000 ohms.
K = relay and mechanical counter.

The counters do not function properly when the radioactivity is too intense, and scaling circuits have been devised in multiples of 2, so that only every fourth, sixteenth, etc., impulse is counted.

Heavy Isotopes

Tracer experiments with heavy isotopes of hydrogen, nitrogen, carbon, sulfur, and other elements have been carried out. The heavy hydrogen is produced by electrolysis of large quantities of water. Heavy carbon and heavy nitrogen have been produced by the thermal diffusion method in which a gas, methane for example, is placed in a

tall vertical tube through which runs an electrically heated wire. The heavier isotope tends to concentrate at the bottom.[1] Taylor and Glockler[2] obtained an enrichment of C^{13} of about 4 per cent, using a pipe 35 ft. high.

Using the chemical equilibrium method that he developed, Urey has produced heavy nitrogen[3] and heavy carbon[4] in rather high concentrations on a large scale. The nitrogen is concentrated by the passage of ammonia gas upward through a packed tower down which a stream of ammonium chloride solution is passing. The carbon is concentrated in a similar manner with sodium cyanide solution and hydrocyanic acid gas.

The concentration of heavy isotope is determined with a mass spectrometer,[5] using, for example, nitrogen or carbon dioxide. A high order of precision is needed for tracer experiments where the heavy isotope is diluted with much of the normal material, and the construction of a satisfactory mass spectrometer is not easy. The gas is ionized and passed through a slit; the ions are deflected in a semicircle by a powerful magnetic field and caught in a Faraday cage. The current is amplified and registered on a galvanometer. The relative heights of the peaks for the different isotopes is a measure of the relative abundance.

and DICKEL, *Naturwiss.*, **26**, 546 (1938); **27**, 148 (1939).; BREWER and BRAMLEY, *Phys. Rev.*, **55**, 590 (1939).

[2] TAYLOR and GLOCKLER, *J. Chem. Phys.*, **7**, 851 (1939).

[3] THODE and UREY, *J. Chem. Phys.*, **7**, 34 (1939).

[4] HUTCHISON, STEWART, and UREY, *J. Chem. Phys.*, **8**, 532 (1940).

[5] NIER, *Phys. Rev.*, **52**, 933 (1937).

CHAPTER XXVII

PHOTOCHEMISTRY[1]

The first practical requirement in photochemical research is a source of light having sufficient intensity to produce a measurable reaction in a reasonable length of time. In most cases, ultraviolet light or light in the blue end of the visible spectrum is desired. In the ultraviolet, all vessels and windows must be made of quartz.

For quantitative research it is necessary to use monochromatic light and to know the intensity of the light. Perhaps the greatest difficulty in photochemical technique lies in the fact that any means of restricting the light to a narrow range of wave lengths reduces greatly the intensity of the available light. Difficulties in interpretation may arise when these restrictions are not followed.

Sources of Light

Tungsten Filament.—For reactions caused by visible light, a 500- to 1,000-watt tungsten filament lamp is often satisfactory. The intensity of the lamp is maintained at a uniform value by inserting an ammeter in the circuit and adjusting a rheostat by hand so as to keep the current constant.

For high intensities, a 70-volt lamp may be operated on a 110-volt circuit. The life of the lamp is only about 2 hr. under these conditions, but the lamps are not expensive. They are sold with photographic supplies under the name "photoflood lamps."

Automobile headlights operating on a storage battery or a step-down transformer are convenient.

Mercury Arc.—The mercury-vapor arc in quartz is the most convenient and powerful source of light for most photochemical reactions. Its chief fault lies in the fact that there are only a few lines in its spectrum, and it is without effect on those reactions which require inter-

[1] For further material the following references are recommended: NOYES and LEIGHTON, "The Photochemistry of Gases," Reinhold Publishing Corporation, New York (1941); DANIELS, Experimental Technique in Photochemistry, *J. Phys. Chem.*, **42,** 701 (1938); DUGGAR, "Biological Effects of Radiation," Chaps. IV and V, McGraw-Hill Book Company, Inc., New York (1936); FORBES, *J. Phys. Chem.*, **32,** 485 (1928); FORSYTHE, "Measurement of Radiant Energy," McGraw-Hill Book Company, Inc., New York (1937).

mediate wave lengths.

As shown in a later section, however, the small number of lines is advantageous in procuring monochromatic light.

The spectrum of the mercury arc is shown in Fig. 101. The widths are proportional to the intensities.

Several types of mercury arcs are commercially available. The more intense ones operate on direct current and carry several amperes. The lamp is started by tilting, the mercury is vaporized by the arc formed, and the current is then carried by the mercury vapor. As the lamp heats, the vapor pressure of the mercury increases and the resistance of the lamp increases so that it is necessary to decrease the resistance of the rheostat. An ammeter should be included in the circuit. After several minutes, the lamp reaches a steady condition. Care must be taken to connect the positive and the negative terminals correctly as labeled and to prevent, with suitable resistance, the passage of too large a current. *Always* in working with ultraviolet light, it is important to protect the eyes with tight-fitting, effective glasses (welding glasses). Albumins in the eye may be coagulated by ultra-violet light, and the effect is cumulative.

The lamps are expensive, and they deteriorate with age, particularly with high currents. The life of a lamp may be increased by wiping off any dust or finger marks with a little alcohol before starting. If not r e m o v e d, this material may be "burnt" into the transparent quartz surface.

Several lamps are available which operate at higher voltages on alternating current with a transformer and high reactance. The small lamps of the General Electric Company type H4 (100 watts) are inexpensive and convenient when a very intense

light is not needed. They require an inexpensive transformer.
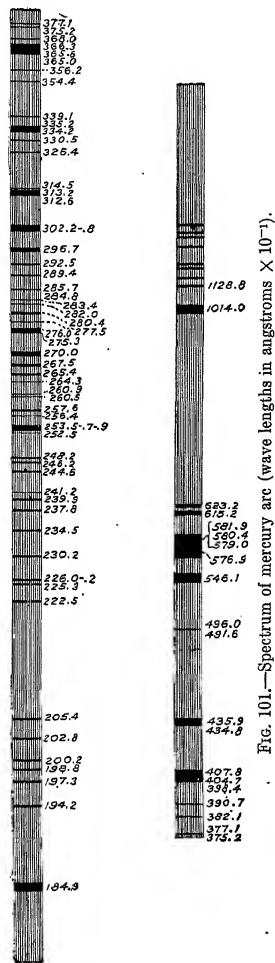
Fig. 101.—Spectrum of mercury arc (wave lengths in angstroms $\times 10^{-1}$).

Left column wave lengths:
377.1, 372.2, 365.0, 366.3, 365.5, 363.8, 356.2, 354.4, 339.1, 334.9, 330.5, 326.4, 314.5, 313.2, 312.6, 302.2-.8, 296.7, 292.5, 289.4, 285.7, 284.8, 283.4, 282.0, 280.4, 276.5, 277.5, 273.3, 270.0, 267.5, 265.4, 264.3, 260.9, 260.3, 257.6, 254.4, 253.5-.7-.9, 252.3, 248.2, 246.2, 244.6, 241.2, 239.5, 237.8, 234.5, 230.2, 226.0-.2, 225.3, 222.5, 205.4, 202.8, 200.0, 198.8, 197.3, 194.2, 184.9

Center column wave lengths:
1128.8, 1014.0, 583.2, 578.2, 581.9, 590.4, 579.0, 576.9, 546.1, 496.0, 491.6, 435.9, 434.8, 407.9, 404.7, 398.4, 390.7, 382.1, 377.1, 375.2

Intense light for illuminating monochromator slits or small cells may be obtained with capillary lamps in which the light is concentrated in a small region.[1] One type can be made from a few inches of capillary quartz tubing with the electrodes set in with sealing wax. The lamp must be run under water. They are so inexpensive that one can afford to run them at a considerable overload, even though their life is short. It is possible to operate such a water-cooled lamp at a kilowatt, even though the arc is confined to a space of only 10 cu. mm. The H6 lamp of the General Electric Company is a very intense water-cooled lamp which operates on alternating current.

"Cold" quartz lamps operating on alternating current at about 6,000 volts give about 85 per cent of all the light at the 2,537 Å line.[2]

Carbon Arc.—Light of high intensity can be obtained with an arc passing between two carbon electrodes arranged to move on a sliding frame as they are used up. The control may be effected automatically with a clock mechanism. The light is not very steady, and frequent renewals are necessary, but the intensity of the blue and long ultraviolet is high. The spectrum contains many bands and a continuous background. Special cored carbons may be purchased,[3] containing one or more salts (such as iron, strontium, nickel, and rare-earth metals), which enrich the spectrum in different regions.

Iron Arc.—The spectrum of this arc contains a great many lines, and the intensity in any one is not great. It is rich in the ultraviolet, and it is perhaps the most convenient source of light for reaching the regions between the mercury lines. The iron arc does not waste away as fast as does the carbon arc. It is usually operated with both electrodes vertical, the upper one (of smaller diameter) being negative. A small piece of titanium steel or tungsten, floating on the top of the lower electrode, serves to keep the arc centered. The brown fumes of the iron oxide are objectionable, and the evolution of heat may cause difficulties. The iron arc is much used in spectroscopy and in the determination of absorption spectra, on account of its large number of well-defined lines.

Other Arcs.—A lamp containing sodium vapor which can be easily attached to the 110-volt alternating current is now available under the name "Sodium Lab-arc." This lamp is much more intense and convenient than the sodium flames heretofore available and is highly recommended whenever monochromatic light is needed for polarimetry or

[1] DANIELS and HEIDT, *J. Am. Chem. Soc.*, **54**, 2381 (1932).

[2] TAYLOR, *J. Chem. Phys.*, **2**, 377 (1934).

[3] "National Therapeutic Arc Carbons," *Bull.*, National Carbon Co., Cleveland, Ohio.

other optical measurements. The light is too weak, however, for most photochemical reactions. The lamp contains a little neon, which ionizes readily and starts the lamp. Full intensity is not reached until the arc has been operating for several minutes. The neon introduces extra lines in the spectrum, but they are weak in comparison with the sodium lines. For most work they constitute no objection, but if necessary they may be removed with the help of suitable filters.

Copper, aluminum, and other metals may also be used as rods to give electric arcs, provided the melting points are not too low. Quartz capillary arcs have been made, using bismuth, cadmium, lead, thallium, and zinc,[1] but they are short-lived.

The hydrogen arc[2,3] is nearly continuous throughout the ultraviolet when it is designed so that the atoms recombine rapidly to give molecular hydrogen. It is valuable for obtaining absorption spectra in the ultraviolet below the range of the tungsten lamp. It is used also for photochemical reactions in the shorter ultraviolet.

Sparks.—For the shorter ultraviolet in the region of 2,000 Å and below, spark discharges between electrodes of aluminum, magnesium, and zinc are used. Several types have been described.[4] It is possible, though troublesome, to obtain from them intensities equal to those of the mercury lamp. Large transformers of 5 to 10 kw. and 10,000 volts are used with large condensers. A blast of cooling air is directed against this spark. The noise and oxide dust are objectionable. Large disks of metal rotating at right angles may be used to confine the arc to one position and yet give constantly fresh surfaces.[5]

Filters, Optical

Glass Filters.—Filters are the cheapest and most convenient means for restricting the radiation to a narrow range of frequencies. A complete assortment is available for use in the visible or longer ultraviolet.[6,7] With them it is possible to isolate many of the mercury lines for photochemical investigations and to use different colors for the photoelectric colorimeter. Intensity of transmitted light is considerably reduced.

[1] HOFFMAN and DANIELS, *J. Am. Chem. Soc.*, **54**, 4226 (1932).

[2] NOYES and LEIGHTON, "The Photochemistry of Gases," Reinhold Publishing Corporation (1941).

[3] MUNCH, *J. Am. Chem. Soc.*, **57**, 1863 (1935).

[4] HOWE and NOYES, *J. Am. Chem. Soc.*, **58**, 1405 (1936).

[5] WIIG and KISTIAKOWSKY, *J. Am. Chem. Soc.*, **54**, 1807 (1932).

[6] "Glass Color Filters," Corning Glass Works, Corning, N. Y.

[7] International Critical Tables, Vol. V, p. 271, McGraw-Hill Book Company, Inc., New York (1929).

Pyrex glass 4 mm thick transmits light at 3,130 Å, but not at 3,020 Å or below. Corex *D* glass transmits down to 2,960 Å, but absorbs 2,800 Å and below. Blue Purple Corex transmits ultraviolet down to 2,500 Å, but absorbs most of the visible light except the blue. Nickel oxide glasses absorb the visible but transmit the longer ultraviolet. Violet Ultra, 8.5 mm thick, transmits only to 3,650 Å of the mercury spectrum. Window glass transmits down to about 3,500 Å. Noviol
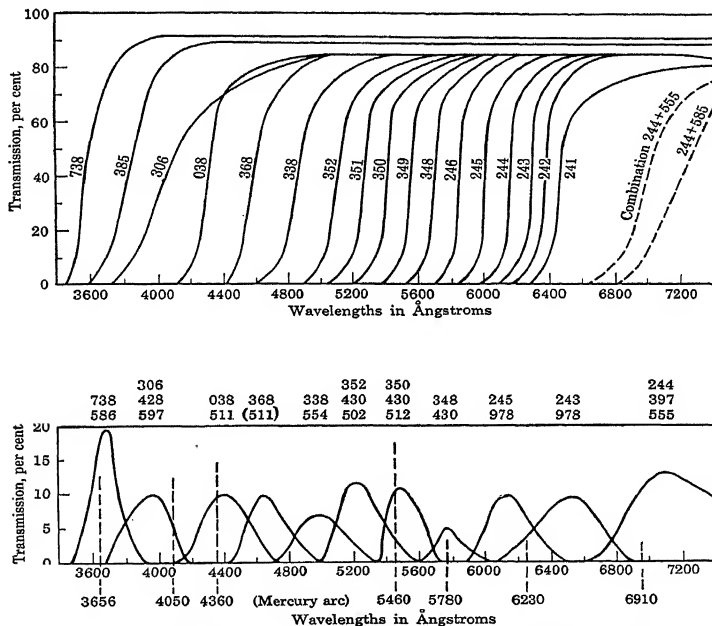
FIG. 102.—Transmission spectra of selected Corning glass filters.

Shade *O* absorbs 3,650 Å, but transmits 4,050 Å. Noviol Shade *C* absorbs 4,360 Å and everything below. For isolating the yellow line of mercury or sodium, Corning filters Nos. 348 and 430 may be used; for the green line, Nos. 350, 512, and 430 are suitable. A thin coating of silver on quartz transmits ultraviolet at 3,130 Å considerably better than light of other wave lengths.

The Corning filters come in standard 2-in. squares and larger. Transmission curves of some of these filters are shown in Fig. 102.

Solutions.—Several solutions and pure liquids have been used for isolated regions of the spectrum, and many more are available for future investigations. Frequently, a combination of two or more filters is effective.

A molar solution of cupric chloride in a glass cell 1 cm thick transmits most of the light between 4,000 and 6,000 Å, and absorbs the remaining light. Addition of calcium chloride narrows the region of transparency up to 4,800 Å, depending on the concentration.[1]

A solution of paranitrosodimethylaniline has absorption in the general region from 3,800 to 4,500 Å.[2] When combined with a cupric chloride filter, it absorbs the visible and transmits some of the ultraviolet just below 3,800 Å.

A concentrated solution of iodine in carbon disulfide is opaque to visible light, but transmits infrared light and heat radiations.

Most of the filters transmit some infrared light. Glass and water absorb the longer infrared, but allow a considerable portion of light in the neighborhood of 1 μ to pass through. A nearly saturated solution of copper sulfate, 2.5 cm or preferably 5 cm thick, has been used for absorbing the infrared. Such a solution absorbs large amounts of the visible light, too.

A set of filters for several lines of the mercury lamp has been assembled by Bowen.[3] The green line of mercury at 5,460 Å is isolated by a 1-cm layer of $CuCl_2 \cdot 2H_2O$ in ethanol (4.57 g per 100 ml) and a 0.5-cm layer of $CuCl_2 \cdot 2H_2O$ in acetone (1.4 g per 100 ml). Only 6.5 per cent of the green light is transmitted.

The line at 4,358 Å is isolated by a 1-cm layer of potassium permanganate in water (0.84 g per 100 ml) and a 0.5-cm layer of $CaCl_2 \cdot 2H_2O$ in water (37.5 g per 100 ml).

The line at 4047–78 Å is isolated with a 10-cm layer of a solution containing 0.44 g $CuSO_4 \cdot 5H_2O$ in 100 ml of $2.7M$ NH_4OH, a 1-cm layer of a solution of 0.75 g of I_2 in 100 ml of CCl_4, and a 2-cm layer of 1 g of quinine hydrochloride in 100 ml of water. The iodine and quinine solutions have to be renewed frequently.

The line at 3,131 Å is isolated by a 3-cm layer of 46 g of $NiSO_4 \cdot 6H_2O$ and 14 g of $CoSO_4 \cdot 7H_2O$ in 100 ml of water and a 1-cm layer of 5 g of potassium acid phthalate in 100 ml of water. The nickel and cobalt must be very pure and free from iron.

[1] Jones and Uhler, *Carnegie Inst. Pub.*, **60**, 213 (1907).

[2] Uhler and Wood, *Carnegie Inst. Pub.*, **71**, 21 (1907); Wood, *Phil. Mag.*, **5**, 257 (1903).

[3] Bowen, *J. Chem. Soc.*, 1935, p. 76.

The line at 2,536 A is isolated by a cm solution of 0.108 g of iodine and 0.155 g KI in 100 ml of water, when combined with the nickel and cobalt sulfate described for the 3,131 Å line.

A filter of chlorine and bromine gas in quartz[1,2] is used for filtering out the longer ultraviolet and leaving the 2,536 Å line of mercury. Acetic acid cuts off all radiation below 2,300 Å.

Christiansen Filter.—The Christiansen filter[3,4] consists of finely pulverized glass in a liquid of practically the same refractive index. That wave length for which the refractive index is the same in the two media passes through, but light of other wave lengths is scattered. It is possible to obtain light within a narrow range by this method. The transmission region can be changed by changing the temperature or the composition of a mixture of two liquids.

If crown glass is used in sizes between 0.3 to 1 mm and immersed in methyl benzoate in a cell 1.5 cm thick, the band of transmitted light will range from 6,800 to 4,600 Å as the temperature is varied from 18 to 50°. A considerable quantity of scattered light is present; but if the light to be transmitted is focused sharply through the filter, much of the scattered light is eliminated from the reaction cell.

The Christiansen filter has been used in the ultraviolet[5] and the infrared as well as in the visible.[6]

Monochromators

In general, the undesired wave lengths can be refracted to one side with a prism more effectively than they can be absorbed in a filter. A spectrometer system which is arranged to supply radiation of a narrow range of frequencies is called a "monochromator."

If a continuous light source is used, there may be some overlapping of adjacent regions, and for this reason a discontinuous spectrum, such as that of mercury arc, is particularly advantageous for use with the monochromator.

These instruments can be purchased directly for visible light (glass), for ultraviolet (quartz), or infrared (rock salt), or they can be built up in the laboratory. The handicap of low intensity can be offset in part by long exposures, by using larger prisms and lenses, and by using

[1] Peskov, *J. Phys. Chem.*, **21**, 382 (1917).

[2] Oldenberg, *Z. Physik*, **29**, 328 (1924).

[3] Christiansen, *Ann. Physik*, **24**, 439 (1885).

[4] Duggar, "Biological Effects of Radiation," Chaps. IV and VII, McGraw-Hill Book Company, Inc., New York (1936).

[5] Kohn and Fragstein, *Physik. Z.*, **33**, 929 (1932).

[6] Barnes and Bonner, *Phys. Rev.*, **49**, 732 (1936).

capillary arcs of greater intensity.   Energies up to 20,000 and 100,000 ergs per second, at different wave lengths of the mercury spectrum, have been obtained with a purity of 98 per cent and more.[1]   A double monochromator giving radiations of high purity has been described.[2]

A monochromator suitable for photochemical investigations in the visible spectrum may be made from a hollow glass prism (15 cm on an edge) filled with ethyl cinnamate.   This liquid has a high refractive index, and it does not deteriorate with use.   A plane glass mirror silvered on the front is placed parallel to the base of the prism, as shown in Fig. 71.   This arrangement, known as the "Wadsworth mounting," has the advantage that, when the prism is set for minimum deviation with sodium light or other monochromatic light, light of any other wave length is brought to the exit slit by merely rotating the prism.   An intensive water-cooled capillary lamp is placed behind a slit at the focus of the lens (20 cm focus and 15 cm diameter), and the parallel light is refracted by the prism and focused on the slit by a second lens of the same dimensions.   After passing through the exit slit, the light is rendered parallel with a convex lens located at a distance such that the slit is at its focus.   The light then passes through the reaction cell in a thermostat and on to a thermopile.   Adjustments are made with a fluorescent plate of uranium glass or a paper previously dipped in benzene and anthracene.   Final adjustments can be made for maximum deflection with the thermopile.   With a monochromator of this type and a quartz capillary lamp of mercury (page 393) using slits of 1 mm, the separation of the 4,360 and 4,050 Å lines was more than 5 mm.   The energy of light was over 25,000 ergs per second on the line at 4,360 Å, and it dropped to less than 1 per cent of this value when the monochromator was turned to a position at either side of this line.

A large monochromator using a water prism may be constructed cheaply, but the resolution is not high.[3]   Liquid prisms should be thermostated if it is necessary to prevent distortion of the lines.

The efficiency of a monochromator may be indicated by introducing a piece of glass which absorbs the line being tested and all the light of shorter wave lengths.   If the light is truly monochromatic, there should be practically no radiation coming through under these conditions.

[1] HEIDT and DANIELS, *J. Am. Chem. Soc.*, **54**, 2384 (1932).
[2] FORSYTHE and BARNES, *Rev. Sci. Inst.*, **4**, 289 (1933).
[3] HARRISON, *Rev. Sci. Inst.*, **5**, 149 (1934).

In the focal isolation method the light of different wave lengths is separated by refraction with a lens instead of a prism. The light of short wave lengths is brought to a focus closer to the lens and passes through a small hole in a plate, while the longer rays are stopped. The apparatus is simpler to construct, and in the short ultraviolet it is probably more effective. This method has been compared critically with the monochromator.[1]

Thermopiles

Not only should the light be monochromatic, but its intensity should be measured. A thermopile is the best apparatus for this purpose.

Construction.—A thermopile is made of a number of thermoelements arranged in series with blackened metal receivers attached to the hot junctions. Radiations of any wave length are absorbed by the black receivers and converted into heat so that the temperature of the junction is raised above that of the corresponding junction at the side of the slit.

The elements are chosen so as to give a maximum thermoelectric effect with a minimum of heat conductance between the two junctions. The material should be as thin as possible without being too fragile. Bismuth-silver thermopiles are often used, but copper-constantan in very thin strips[2] and platinum-tellurium elements are satisfactory. Bismuth and bismuth alloyed with 5 per cent of pure tin are recommended by Cartwright. Detailed instructions for constructing thermopiles are given by Cartwright and Strong.[3] The construction of a small thermopile has been described by Beckmann and Dickinson.[4] The theory and practice of thermopile construction have been discussed critically by Leighton and Leighton.[5]

The ordinary linear thermopile is smaller than the chemical reaction cell behind which it is placed, and it is necessary to move the thermopile over the whole area in order to obtain an average value. Large-area thermopiles which do their own integrating are simpler for photochemical investigations. The thermocouples, thoroughly protected with glyptal lacquer, are attached with de Khotinsky cement to the

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[1] HEIDT and FORBES, *Rev. Sci. Inst.*, **5**, 253 (1934).

[2] MOLL and BURGER, *Z. Physik*, **32**, 575 (1925).

[3] STRONG, "Procedures in Experimental Physics," Prentice-Hall, Inc., New York (1939).

[4] BECKMANN and DICKINSON, *J. Am. Chem. Soc.*, **52**, 126 (1930).

[5] LEIGHTON and LEIGHTON, *J. Phys. Chem.*, **36**, 1882 (1932).

back of a blackened receiver 10 by 40 mm in area of sheet silver 0.02 mm in thickness, as shown in Fig. 103.   Fine copper and constantan ("Ideal") wire is chosen which with the 20 to 50 junctions will give the correct resistance to critically damp the galvanometer to be used.   The junctions are soldered with pure tin, using rosin for a flux and removing all excess tin.   The thermocouples and receiver are attached to a bakelite frame which is then set into a rectangular block of aluminum or other metal.   Corrections for the absorption by the quartz window are obtained by interposing a second window like the first and determining the percentage of the light transmitted.

The thermopile is connected directly to the galvanometer, and the deflection is proportional to the current through the galvanometer,
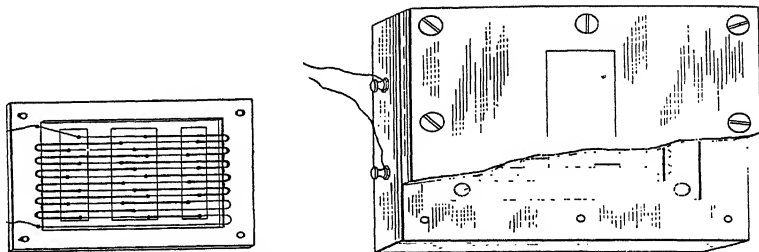
FIG. 103.—Construction of large-area thermopiles.

which, in turn, is proportional to the voltage generated by the difference in temperature of the junctions at the center and side of the thermopile.   The temperature difference is proportional to the energy of radiation falling on the receivers.   The receivers are covered with lampblack, together with a little platinum black to increase the heat conductance.   The mixture is suspended in methanol containing a trace of shellac, applied to the receiver, and allowed to evaporate.   The black surface is practically nonselective, converting radiation of all wave lengths directly into heat.   This is the chief advantage over photoelectric cells.

The thermopile should have a resistance equal to the critical damping resistance of the galvanometer so that a quick return to the zero reading is obtained.   The galvanometer scale is arranged to slide back and forth so that it may be set at zero conveniently before each reading. Potentiometers are not often used with thermopiles because the drift of the zero reading is so great.   The drift is caused by thermal inequalities in the thermopile, which are accentuated by a changing room

temperature or drafts. Evacuation not only improves the constancy
of the zero point, but it may increase the sensitivity several fold.

Calibration.—The deflection of the thermopile-galvanometer sys-
tem is sufficient for comparative results, but for investigations connect-
ing the quantity of chemical reaction with the energy absorbed
(molecules per erg or per quantum), deflections are converted into
absolute units. The quantity of radiation falling on the thermopile is
obtained in ergs per second (or watts) by calibration with a carbon-
filament lamp standardized at the National Bureau of Standards.[1]
The apparatus is shown in Fig. 104. The standard lamp L is connected
to storage batteries or other steady source of direct current, and the
rheostat R is adjusted until the ammeter M gives an exact reading
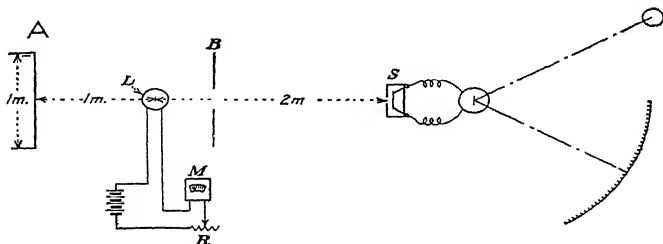
Fig. 104.—Calibration of thermopile.

corresponding to one of the values given in the calibration table accom-
panying the lamp (*e.g.*, 0.4 amp.). A black screen A, 1 m square, is set
100 cm back of the lamp, and another one B, having a square hole
25 cm on a side, is set 25 cm in front of the lamp with the opening
directly in front of it. The thermopile slit is mounted exactly 200 cm
from the tip of the lamp. The lamp is rotated so that the two lines
etched on either side of the globe are in line with the thermopile, giving
the same conditions as used in the standardization. The room must be
dark, free from objects that may reflect light on the thermopile S, and
the operator must remain at a considerable distance.

The slit is narrower than the thermopile receivers, and its area must
be accurately determined. If there are horizontal gaps between the
receivers, a correction for the area must be made. The effective area
is multiplied by the radiation in watts per square millimeter as given on
the calibration sheet.

[1] These lamps may be purchased at a nominal cost from the National Bureau
of Standards. The calibration is described by Coblentz,
11, 87 (1915).

The following data illustrate the calculation:

Galvanometer deflection with standard lamp (s) = 28 mm.

Galvanometer deflection with monochromator (g) = 400 mm.

Radiation from standard lamp = 5.4 ergs per second per square millimeter, under conditions specified by the Bureau of Standards.

Area of slit (a) = 13.5 sq. mm.

Time of radiation (t) = 2,250 sec.

$$\text{Total radiation, } E = \frac{g}{s} \times a \times t \times 5.4$$

$$= \frac{400}{28} \times 13.5 \times 2,250 \times 5.4 = 2,340,000 \text{ ergs}$$

Bolometers

The bolometer is essentially a sensitive Wheatstone bridge with the two arms consisting of strips of thin platinum foil, placed side by side. One of the strips is blackened, and when it is exposed to radiation, its resistance is raised and the galvanometer is thrown out of balance. The increase in resistance of the foil is proportional to the rise in temperature, which in turn is proportional to the energy impinging on it. The bolometer is capable of great accuracy. Descriptions are given by Abbott[1] and Coblentz.[2] The classic researches of Langley on solar radiation were carried out with the bolometer. It is not often used in photochemical investigations.

Photoelectric Cells

When light of short wave lengths strikes the surface of potassium or other alkali metals (or their hydrides), electrons are emitted and they conduct current across the evacuated space to a positive wire. A radio battery of 90 to 180 volts is connected to the cell through a galvanometer, and the deflection of the galvanometer is proportional to the intensity of light.

The photoelectric cell is the most sensitive detector of radiation, but it is less valuable in photochemical research than the thermopile because it is selective, *i.e.*, it responds more to some wave lengths than to others. In fact, red and infrared light may not affect it. The spectral sensitivity of photoelectric cells is dependent on the particular alkali metal used, the metals of higher atomic weights being more sensitive for longer wave lengths. The sensitivity of the photocell is unnecessary for much photochemical work because a considerable quantity of energy is required to give a measurable chemical reaction.

[1] Abbott, *Astrophys. J.*, **18**, 1 (1903).

[2] Coblentz, *Bur. Standards Bull.*, **11**, 171 (1914).

One of the important uses of the commercial photoelectric cell is the automatic control of various operations by the operation of relays and accessory apparatus. The arrangement for this purpose is shown in Fig. 105. When light strikes the photoelectric cell A, the current from the battery B is increased, and the potential drop across the electron tube C is increased. This increase in voltage increases greatly the current in the second circuit, and the armature of the relay R is attracted. The spring of the relay is stretched so that the relay is kept open except when the current is increased by the light on the photoelectric cell. The relay can operate a bell, burette, electric heating coil, or other laboratory device. Several practical photo relays[1] are now on the market.

Photoelectric cells and amplifiers for laboratory work are discussed fully by Strong.[2]
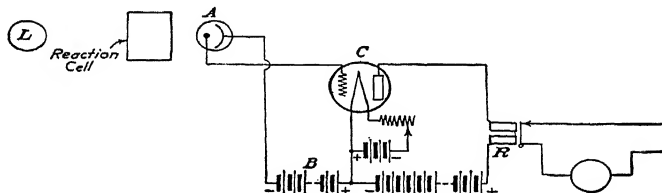
Fig. 105.— Photoelectric cell and relay.

Although the photoelectric cell is selective in its response to radiation, it can nevertheless be used in some photochemical work. The fact that it does not respond to the longer wave lengths is advantageous in certain cases. For example, if a filter is available to cut off light of shorter wave length than that of the specified region, and the photocell does not respond to light of longer wave lengths, the arrangement is as satisfactory as a monochromator for the particular measurement. The photoelectric cell and galvanometer circuit may be calibrated against a sensitive thermopile using monochromatic light to which the photoelectric cell is sensitive. The thermopile in turn is calibrated with white light from a carbon lamp as described on page 401.

By introducing a photoelectric surface the Geiger-Mueller chamber, described on page 388, may be adapted to respond to ultraviolet light as well as to radioactivity. It becomes then the most sensitive detec-

[1] "Electronic Devices for Industry," General Electric Company, Schenectady, N. Y.

[2] STRONG, "Procedures in Experimental Physics," Chap. X, Prentice-Hall, Inc., New York (1939).

tor of light and has found use in experiments on feeble luminescence and fluorescence.

Reaction Cells

Flasks or open dishes may be used for qualitative work. In precision work, the cell has front and back plates of polished quartz or glass, and the cell is placed between the exit slit of the monochromator and the thermopile.

Quartz is transparent throughout the whole visible and ultraviolet range down to 2,000 Å. Pyrex in 2 mm thickness will transmit 10 per cent at 3,000 Å, whereas "Corex" will transmit 10 per cent at wave lengths as low as 2,700 Å. "Pyrex Vycor" glass contains 96 per cent silica and is fairly transparent as low as 2,500 Å.

In some cases, the cell may be made from plates of glass or quartz held together with sealing wax, water glass, or other material, depending on the chemical activity of the reacting system. Rectangular or cylindrical cells may be made by fusing together plates of pyrex, or of quartz. The photoreaction may be followed by withdrawing samples and analyzing, by measuring pressure changes, by determining the absorption of light, or by various other means.[1] The best results are obtained when the beam of light fills nearly the whole volume of the cell.

Corrections for the light reflected at an interface are necessary in accurate work. The light should strike the windows at right angles, but even under these conditions about 4 per cent of the light is reflected at each quartz-air surface. The light reflected at a quartz-water or glass-water surface is practically negligible. The fraction of light reflected at right angles is given by Fresnel's formula

$$I_r$$

where I_r and I_i refer to the intensity of the reflected and incident light, respectively, and μ is the ratio of the refractive indices of the two media.

The light entering the inside of the reaction cell is greater than that registered on the thermopile receivers, by an amount that depends on the number of quartz-air (or glass-air) surfaces lying between them. Sometimes the light reflected from the thermopile window passes back through the cell. The corrections are usually small, and they vary with the particular arrangement of cells and thermostat windows. Usually the corrections can be made to cancel out, in gas reactions, by

[1] FORBES, KISTIAKOWSKY, and HEIDT, *J. Am. Chem. Soc.*, **54**, 3247 (1932); DAMON and DANIELS, *J. Am. Chem. Soc.*, **55**, 2364 (1933).

placing an empty cell in the path of the light when a zero reading is made. The difference in energies registered on the thermopile gives the energy absorbed. In the case of solutions, the amount of light absorbed is obtained by subtracting the galvanometer reading with solution in the cell from the reading with pure solvent in the cell. It is a great convenience to have two cells exactly alike, either one of which may be slid into the path of the light.

Photography

For photography in the ultraviolet and infrared, special plates are required. For the near ultraviolet, the ordinary spectrum plate may be used, but for the extremely short wave lengths, below 2,500 Å, the absorption of light due to the gelatin becomes marked, and below 1,860 Å the plate is of no value. Schumann has developed a plate for ultraviolet photography which has enabled him to photograph spectra down to 1,180 Å. The Schumann plate has an exceedingly thin layer of gelatin carrying a relatively high concentration of very fine grains of silver bromide. The advantages of the Schumann plate over the ordinary plate begin to show up at about 2,200 Å and become more and more marked with decreasing wave length. The range of the ordinary plate can be increased somewhat by coating it with a very thin layer of a fluorescing mineral oil. Wherever ultraviolet light strikes the oiled surface, fluorescence is produced, and this fluorescent light, being of longer wave length, produces a developable image of the slit of the spectrograph.

The ethyl carboxylic ester of dihydrocollidine is even better than a fluorescent oil. This substance is dissolved in a suitable organic solvent, and the plate is bathed therein and allowed to dry. The microcrystalline deposit fluoresces strongly in the ultraviolet.

Special sensitized plates, known as "spectrum plates," are used for photographing the visible part of the spectrum. For the extreme red and infrared, we now have available plates sensitized with kryptocyanin, neocyanin, mesocyanin, and xenocyanin. Kryptocyanin-sensitized plates are useful in the range 7,000 to 8,000 Å, with a maximum sensitivity at 7,500 Å. Neocyanin sensitizes for the range 7,200 to 9,100 Å, with a maximum at 8,300 Å; but with long exposures it can be used out to 10,000 Å. Mesocyanin sensitizes from 6,800 to 9,400 Å, with a maximum at 8,800 Å; and xenocyanin sensitizes from 7,700 to 10,300 Å, with a maximum at 9,400 Å. Recently, the Ilford Company, of England, has produced a new infrared plate which has a very satisfactory speed and which works very simply. It is sensitive up to 9,000 Å, with a maximum sensitivity at 8,100 Å. For general photographic

work in the infrared, the xenocyanin plates are not so useful as the mesocyanin. They are less sensitive in the region from 8,000 to 9,000 Å, and, furthermore, they are so unstable that they must be kept in an ice box. Both the mesocyanin and xenocyanin plates should be hypersensitized before use. They are placed for a short time in 4 per cent ammonia at 10°C. and dried rapidly. This increases the sensitiveness about tenfold.

It is possible to use a Wratten Series No. 3 safelight with the Eastman Extreme Red-Sensitive (Type 3-R) and Mesocyanin (Type 3-P) plates. Xenocyanin (Type 3-Q) plates must be developed in total darkness.

Infrared plates of sufficient speed to take pictures from airplanes have been produced. Pictures of mountains over 330 miles distant have been taken from an airplane, at an elevation of 23,000 feet. Infrared photography has already been used to good advantage in the examination of old documents, suspected forgeries, old paintings, old writings on leather, in photomicrography, in studying skin diseases, in the examination of textiles, and in spectroscopy. Doubtless many other applications will be found.

Naturally, no substances transparent to infrared radiations can be used in the construction of the camera and plateholders. Ordinary leather cannot be used for the bellows of the camera, as it is transparent; it must be covered with some substance opaque to these rays. Metal slides should be used in the plateholder. In the dark room, precautions must be taken that infrared rays from the safelight are not permitted to strike the plates.

Photomicrography.—It has long been known that higher resolution is obtained by the use of light of short wave lengths, and ultraviolet photomicrography has been practiced for many years. One of the chief difficulties has been that of focusing the image properly, particularly at high magnifications.

It has been shown that excellent results may be obtained by use of the 3,650 Å line of the mercury arc.[1] Theoretically, with an objective of N.A. = 1.40, there should be a gain of 19 per cent in resolving power by substituting this light for that passed by a Wratten C filter. The neighboring weaker lines can be eliminated by using a Wratten No. 18A filter, as this has a maximum transparency at 3,630 Å, and transmits 38 per cent of the 3,650 Å line. Two special objectives have been worked out, a 16-mm and an oil-immersion of 1.7 mm focal length in which achromatism has been accomplished for the two lines

[1] Abridged Scientific Publications from the Kodak Research Laboratories, vol. 15, 101 (1931–1932).

3,650 A (ultraviolet) and 5,460 A (visible). To examine the object being photographed, it is illuminated with light coming through a green filter No. 62 or 77. After the focus has been obtained, the green filter is replaced with the No. 18A filter, and the photograph taken. The focus is not only sharp, as thus obtained, but often many details invisible to the eye appear in the photograph taken by the ultraviolet light. If the oil-immersion objective is to be used, the cedar oil customarily used should be replaced by sandalwood oil, as it transmits ten times as much light.

For ordinary photomicrography, the Wratten M plate is recommended. If greater speed is desired, for photography in the visible part of the spectrum, the Wratten Hypersensitive Panchromatic plate should be used. Although this plate has a higher sensitiveness in visible light than does the Eastman Speedway plate, for the 3,650 Å radiation this condition is reversed, the Speedway plate being about three times as fast. For low intensity, this latter plate should be used.

PART III
MISCELLANEOUS OPERATIONS

CHAPTER XXVIII

CALIBRATION

Weight, Volume, and Length

Weight.—The chemical balance is an instrument capable of very great accuracy when it is properly used. There are analytical balances, Chainomatic balances, damped balances, assay balances, semimicrobalances, microbalances, etc. After being placed in position a balance should be leveled and tested for adjustment and sensitivity. The sensitivity of a balance is the displacement of the resting point produced by an excess of 1 mg on either side of the balance. It should not, within reasonable limits, vary with the load on the balance. Its definition involves the zero point, which is found in the following manner: The beam is released and allowed to swing freely. Readings are taken of the extreme points of the scale reached by the pointer, the average of three successive readings on one side of the center being compared with the intervening two readings on the other side. If this average is the same as that of the two readings on the other side of the center, the zero point of the scale is correct. If the average of three is greater than that of the two readings on the other side, the zero point of the balance is toward the side on which three readings were taken; and if the average is less than that of the two readings on the other side, the reverse is true. The zero point of a balance may be corrected by means of the adjustment screws at the ends of the beam; however, it is necessary to do this only in case the zero point is considerably removed from the center.

Having determined the zero point, the sensitivity of the balance is determined by placing an excess of 1 mg, by means of a suitable rider, on one side of the balance and again determining the zero point. The displacement of the zero point is the measure of the sensitivity. To determine the manner in which the sensitivity changes with load, equal weights, e.g., 1, 10, 20, or 50 g, may now be placed on each pan, without removing the 1 mg excess on one side, and the displacement of the zero point may be redetermined. This method assumes the weights to be relatively exact.

No matter what the possibilities of a particular balance may be, a weighing cannot be considered accurate unless the weights used have been standardized. The usual method of standardizing a set of weights is that due to Kohlrausch,[1] although the method proposed by Richards[2] has certain advantages. In the latter method the weights to be standardized are weighed wholly on one side

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[1] KOHLRAUSCH, "Praktische Physik," B. G. Teubner, Leipzig (1935).

[2] RICHARDS, *J. Am. Chem. Soc.*, **22**, 144 (1900).

of the balance, the comparison being made by substitution. This method eliminates any inequality in the length of the arms of the balance which must otherwise be computed; in addition, it obviates any confusion resulting from the interchange of weights from one pan to the other. The procedure of Richards gives values that are identical with those to be found by substituting in algebraic formulas like those of Kohlrausch.[1]

The Kohlrausch method is as follows: The 50-g weight is compared with the sum of the others, having previously determined the zero point of the balance by the method of oscillations. If the 50-g weight is placed on the left pan and the others on the right pan, it is necessary to determine what weight, if any, must be added to the weights on the right or left in order to obtain an exact balance. The weights are now interchanged, the 50-g weight being placed on the right and the other weights on the left, and the weight necessary to restore the balance is thus obtained. The following equations, representing the above data, permit the calculation of the ratio of the balance arms:

$$50 = 20 + 10' + 10'' + 5 + 2 + 1' + 1'' + 1''' + r \text{ g}$$
$$20 + 10' + 10'' + 5 + 2 + 1' + 1'' + 1''' + l \text{ g} = 50$$
$$\therefore 50 = 20 + 10' + 10'' + 5 + 2 + 1' + 1'' + 1''' + \tfrac{1}{2}(r + l)$$

Also, the ratio of the balance arms R/L is given by the expression

$$\frac{R}{L} = 1 + \frac{(l - r)}{100}$$

The value R/L will be found to vary slightly with the load; therefore it should be determined for several different loads. The value found with 10 g on each scale pan may be used for the comparison of the smaller weights.

In the manner described above, the other weights of the set are compared among themselves. In this way, the relative values of the different weights are obtained.

By comparing any one of the pieces, preferably one of the larger ones, with a standard weight, the correct values of each of the pieces may be computed.

For all exact work in physical chemistry, weights should be corrected for the buoyancy of the air. In this manner, there is obtained the weight that the body would have if weighed in a vacuum. Using brass weights, the correction is given by the equation

$$1 + \frac{0.0012}{\cdot} - \frac{0.0012}{8.5}\Big)$$

where W_0 = the true weight.
$\quad W$ = the apparent weight, given by the brass weights.
$\quad d$ = the density of the body being weighed.
$\quad 0.0012$ = the density of air.
$\quad 8.5$ = the density of weights.

[1] Eaton, *J. Am. Chem. Soc.*, **54,** 3261 (1932).

Having standardized the operations of weighing, the calibration of volumetric flasks, pipettes, and burettes follows without great difficulty, since the true milliliter is the volume of 1 g of water at 4°C., the weight being reduced to *vacuum*.

Volume.—When volumetric apparatus is to be used for the purpose of preparing solutions of definite concentration, it must be graduated in true milliliters. In determining a given volume, the procedure is to determine the weight of boiled distilled water, at a definite temperature and corrected to *vacuum*, which is required to fill that volume. The density of the water at that temperature is obtained from standard tables. To calibrate a flask, it is first thoroughly cleaned and dried, after which it is counterpoised on a balance. Boiled distilled water, having a predetermined temperature, is run into the flask until the lower edge of the meniscus just touches the mark on the neck of the flask. After removing any water in evidence above the column of liquid with filter paper, the weight of the water is determined. For the purpose of calibrating the larger flasks, special large-capacity balances should be used. The volume of the flask is given by the equation

$$V = \frac{M}{D}$$

where V = the volume of flask.

M = the mass of water.

D = the density of water.

In calibrating a pipette to deliver a given volume, certain precautions must be observed. The pipette must be scrupulously clean. Volumetric glassware is not clean when water wets it in droplets. The pipette must be allowed to deliver in exactly the same way each time, a good way being to place the tip against the inside wall of the vessel into which the liquid is being delivered and allow the liquid to drain itself for a specified length of time. Many delivery flasks, pipettes, and burettes are calibrated for both delivery time and temperature, as marked on the piece of apparatus. The actual calibration is similar to that of a flask. Boiled distilled water is drawn up into the pipette to the mark, and the weight of the water delivered is determined. If this weight is greater or less than the desired amount, a strip of gummed paper with straight edge is placed below or above the original mark. The weight of water delivered when the lower edge of the meniscus is at the new mark is now determined. The difference between the weighings and the distance apart of the original and temporary marks will indicate the position for a third mark (the volume desired), if this is necessary. The correctness of the final position of the mark should be determined by check weighings.

To calibrate a pipette for withdrawing a certain volume of liquid, a stoppered flask containing boiled distilled water is weighed, water is withdrawn from the flask to a mark on the pipette, and the weight of water withdrawn determined by reweighing the flask. The correct position of the mark on the pipette is determined by trial in a manner exactly analogous to that described in the calibration of the pipette to deliver a given volume.

The Richards[1] modification of the method of Ostwald,[2] in which a calibrator of any size may be used, is suggested for the calibration of a burette. Using the calibrator, it is necessary to compare, in parallel columns, its multiples with the actual readings of the burette. The capacity of the calibrator is found in the following manner: An integral number of fillings of the calibrator from the burette being calibrated will correspond to a certain volume on the burette. If the burette is now refilled and exactly this amount of boiled distilled water is run out into a weighed flask, the weight of the water gives (making suitable corrections for the density of the water and for the buoyancy of the air) the true volume of the integral number of fillings of the calibrator. Dividing this volume by the number of fillings gives the true volume of the calibrator. Suppose this volume to be 5.25 ml, then the differences between the successive readings of the burette and the successive numbers 5.25, 10.50, 15.75 . . . etc., give the errors of graduation of the burette at these points. It is convenient in using the burette to have these differences plotted against the volumes, thus giving a true calibration curve of the burette.

<p style="text-align:center">80   .   90   .</p>

<p style="text-align:center">0   5   10</p>
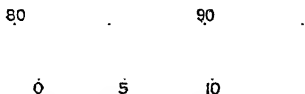
<p style="text-align:center">Fɪɢ. 106.—Vernier scale.</p>

Length.—The determinations of length in physical chemistry, although not so universal as those of weight and volume, are nevertheless important. The standard of length is the meter, which may be defined as the distance between two marks on a platinum-iridium bar which is kept in Paris. Exact copies of this bar are in existence in standard laboratories all over the world. For practical scientific purposes, the one-hundredth part of a meter, the centimeter, is used as the unit of length.

Rules are prepared by means of dividing engines, materials such as wood, celluloid, glass, steel, and silver being used. The engine is arranged so that every fifth and every tenth mark made is longer than the regular marks. The marks are scratched or cut into the bar so that they will be permanent. In the case of glass scales, the marks may be made with a diamond point, or by etching the glass with hydrofluoric acid in grooves cut in a paraffined surface. It is, of course, necessary that the dividing engine be tested before it can be used. The methods are difficult and cannot be described here.

Microscales are prepared in several ways. They can be obtained by photographic reduction of larger scales or by means of diffraction-grating machines. They are usually used in conjunction with specially designed measuring microscopes called "comparators."

, *J. Am. Chem. Soc.*, **21**, 527 (1899).
[2] Oꜱᴛᴡᴀʟᴅ–Lᴜᴛʜᴇʀ–Dʀᴜᴄᴋᴇʀ, "Physiko-chemische Messungen," 5th ed., p. 91, Akademische Verlagsgesellschaft, Leipzig (1931).

Thickness and diameters are measured by means of micrometers. The so-called outside micrometer is used to measure outside diameters, whereas the inside micrometer is designed so that inside diameters may be measured. These instruments are fitted with screw threads and direct-reading scales.

In order to increase the accuracy of the reading of a scale, the vernier is frequently used. If it is desired to read to the nth part of an interval, the distance of $(n - 1)$ divisions is divided into n parts on the vernier. If the zero point of the vernier is placed opposite the length to be measured, it is necessary simply to look along the divisions of the vernier until one, m, is found, which is in exact juxtaposition with a division on the scale. Then the zero point of the vernier is m/n units beyond the last division of the scale. The explanation will be clarified by a consideration of Fig. 106. In the diagram n, the number of divisions on the vernier $= 10$, corresponding to $(n - 1) = 9$ divisions of the scale. Division 3 of the vernier coincides with one of the divisions of the scale. Therefore, since the zero point of the vernier lies between 81 and 82, the reading is 81.3. Such instruments as calipers, barometers, and polarimeters are practically always equipped with verniers.

Another instrument used in measuring length, or, more correctly, height, is the cathetometer. It consists of a telescope mounted exactly horizontally on one part of a divided metal block, which in turn is mounted on a vertical pillar. The block slides up and down the pillar, and can be locked at any desired point. The telescope can be moved upwards or downwards, within certain limits, by means of a worm gear. To ensure the pillar being in a truly vertical position and the telescope in a truly horizontal position, both are provided with delicate spirit levels.

In the eyepiece of the telescope there is a cross hair which can be placed in a horizontal position, the vertical cross hair aiding in this setting. To measure a height, the worm gear is operated until the cross hair coincides with the upper mark to be read, and the position of the zero of the vernier (on the block carrying the telescope) with respect to the scale on the pillar is read. The cross hair is then set on the lower mark, and a similar reading on the scale is made. The difference gives the height desired. The telescope may also be provided with an additional horizontal cross hair (or a pair of them), operated by a micrometer adjustment, by means of which an additional decimal place may be determined.

The vertical scale on the pillar should be made of invar, an alloy having a negligible temperature coefficient.

Ocular micrometers for compound microscopes are useful for measuring the size of extremely small particles.

CHAPTER XXIX

THERMOSTATS

Ice Bath.—The simplest type of thermostat is represented by an ice bath, in which the melting or freezing of ice offsets any external thermal effects. Certain precautions are necessary to maintain an ice bath at exactly 0°C. The ice must be pure, and finely shaved, and the spaces between the particles
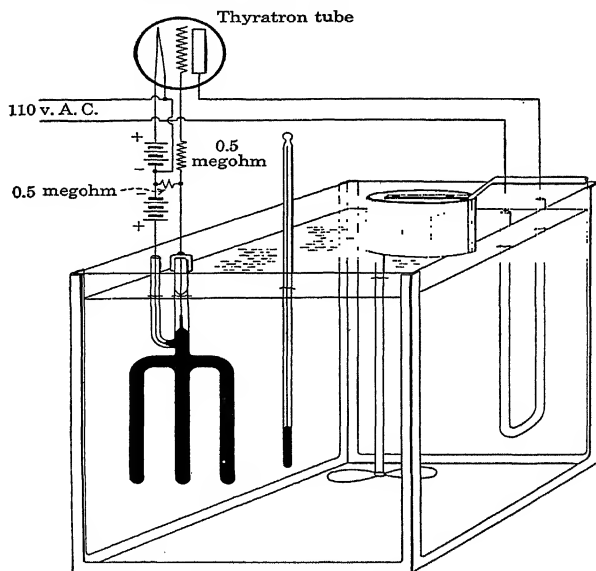
FIG. 107.—Thermostat.

must be completely filled with pure water. It is important to have the pieces of ice fill the whole vessel. In case there are any regions which are not completely filled with pieces of ice, vigorous stirring of the whole bath is essential. For precision work, the mixture of fine ice and water should be surrounded by a secondary ice bath to minimize melting, and the ice should be frequently rinsed with pure water, chilled to 0° to remove any soluble material released by the melting ice.

Electrical Thermostats.—A water bath maintained automatically at a constant temperature with intermittent electric heating is one of the most important pieces of equipment in a physical-chemistry laboratory. The principle of operation is shown in Fig. 107. When the bath cools below a predetermined temperature, the liquid in the regulator contracts sufficiently to lower the mercury in the capillary tube away from contact with the wire. The electrical circuit is thus broken, the electromagnet ceases to operate, and the spring pulls the armature back so as to close the heating circuit. The water bath is heated, and the liquid in the regulator expands until the mercury again contacts the wire and closes the circuit. When this circuit is closed, the electromagnet attracts the armature and breaks the heating circuit. This alternate closing and opening of the heating circuit continues indefinitely and maintains the temperature within a narrow range.

The thermostat vessels may be made of sheet copper or of painted iron. Large glass jars, such as storage battery jars, are convenient for certain measurements such as those of viscosity, where a transparent bath is necessary. Thick glass plates may be set into an iron frame with a cement made from litharge and glycerin. The stirrer is operated with a slow motor or with a motor and step-down pulleys. The heating may be accomplished with a commercial heater in the form of a long rod or flat strip covered with metal, or simply with an electric light bulb partly immersed in the water. The ordinary lighting circuit of alternating current at 110 volts is usually used.

The regulator may be filled entirely with mercury, or an inverted bulb may be used with purified toluene which has a greater coefficient of expansion. The temperature control over a long period of time is better without the toluene.

Bimetallic thermoregulators utilize the difference in expansion of two metals. Although very simple and inexpensive, they often give adequate control to a fraction of a degree, even without a relay. An inexpensive regulator arranged in the form of a spiral which will regulate up to 300° is now on the market.

A regulator (Fenwall) is available in which two metal strips buckle, when they expand with temperature, and bring two contacts together which close the heating circuit. The whole unit is enclosed in a thin metal cylinder and immersed in the thermostat bath. A current of 10 amp. is handled without a relay and the regulation is good to 0.1 to 0.5°.

Commercial regulators are now available in which a suitable liquid with a boiling point in the range to be covered is sealed off with solder in a flexible bellows of very thin copper, known as a "sylphon bellows." The large change in vapor pressure with a small change in temperature expands the bellows and makes electrical contact. Other regulators use a mercury column.

Since the heating currents are large it is necessary to use large contacts on the relay. Commercial relays with large movement of the contacts are available. Some will operate on the alternating current. A fixed resistance of about five times the resistance of the relay may be connected across the two

contacts to reduce sparking. A rocking switch which makes and breaks a mercury column in an evacuated tube is more reliable.

A simple alternating current relay can be made from parts obtainable for less than $5 at a radio store, thus dispensing with dry batteries or rectifiers. An a-c relay with double contacts (for example, Potter and Bromfield PRA 3) will operate satisfactorily up to 10 amp. A 5,000- or 6,000-ohm resistance is shunted across the thermostat circuit and a 0.5-μf condenser is shunted across the heating circuit.

A thermostat of this type regulates within about 0.01°. Improvements in the regulator can decrease the fluctuations to about 0.002°, but careful design and thorough stirring are necessary to maintain this accuracy throughout the whole thermostat. The regulation can be improved somewhat by operating the contact wire on a slowly moving cam so that it dips below the surface of the mercury in the capillary every few seconds. Any nonconducting scum on the surface of the mercury is thus rendered harmless. A large rotating propeller type of paddle at the bottom near the center of the water bath gives effective stirring. Stirring with a rapid stream of bubbles from a compressed-air line is often satisfactory.

A great many modifications of this standard type of thermostat have been made. The use of an electron tube is advantageous[1] because practically no current is passed through the mercury and a fouled surface is still sufficient to close the circuit through the metallic wire. Thyratron tubes[2] operate in this way, and have such a large current-carrying capacity that an electromagnetic relay with its troublesome electrical contacts is unnecessary. For the most accurate and reliable long-time operation of a thermostat, thyratron tubes are recommended. They eliminate all moving parts and eliminate sparking and corrosion at the thermostat contacts. A thyratron F.G. 17 costing less than $10 will carry up to an ampere of current. Tubes for larger currents are more expensive. Circuits are available which eliminate the batteries shown in Fig. 107. A precision thermostat with thyratron tube and oil bath is described by Beattie.[3] A good thermostat circuit is described by Rudy and Fugassi.[4] If a relay is included in the circuit an inexpensive thyratron may be used.

Excellent thermostats for high temperatures can be made, in which the heating coils are turned on or off by a beam of light from a galvanometer acting on a photoelectric cell and operating a relay.[5]

For many purposes where a thermostatic control to 1° is sufficient, an air thermostat is adequate and more convenient. A box with insulated walls and door may be built similar to those of a commercial refrigerator and provided with a double glass door. An efficient fan is essential.

Vapor Thermostats.—A liquid boiling in a flask or tube provided with a reflux condenser provides a convenient method for maintaining a constant

[1] BEAVER and BEAVER, *Ind. Eng. Chem.*, **15**, 359 (1923).

[2] HULL, *Gen. Elec. Rev.* **32**, 213–223 and 390–399 (1929).

[3] BEATTIE, *Proc. Am. Acad. Arts Sci.*, **69**, 389 (1934).

[4] RUDY and FUGASSI, *Ind. Eng. Chem. Anal. Ed.*, **12**, 757 (1940).

[5] ZABEL and HANCOX, *Rev. Sci. Inst.*, **5**, 28 (1934).

temperature. The vapor thermostat is conveniently heated with an electric heating coil. With low-boiling liquids, excellent results are obtained by placing the vessel in a beaker of water kept a few degrees above the boiling point of the liquid in the thermostat.

A number of the liquids commonly used in these thermostats, with the temperatures to be obtained at 760 mm, are tabulated below.

	Degrees Centigrade		Degrees Centigrade
Ether.....................	34.5	Water.....................	100.0
Carbon bisulfide.............	46.3	Toluene...................	110.5
Acetone....................	56.1	Isoamyl alcohol.............	131.6
Chloroform.................	61.2	Aniline...................	184.4
Carbon tetrachloride........	76.7	Nitrobenzene...............	210.8
Benzene...................	79.8	Mercury...................	356.9
		Sulfur....................	440.0

Excellent results may be obtained by using a barostat (page 310) in connection with a vapor thermostat. Unless a barostat is used, barometric changes may introduce fluctuations of several tenths of a degree. The barostat may be adjusted to give any temperature over a large range by operating at reduced pressure. Nitrobenzene or mercury boiling under reduced pressures with an all-glass apparatus connected to a barostat provides one of the most satisfactory means for thermostating at higher temperatures.[1] Caution is, of course, necessary with mercury fumes.

Sometimes it is possible to dispense with the reflux condenser if the boiling material is inert, noninflammable, and nonpoisonous. For example, a wide tube perhaps 50 cm long is mounted vertically, and a little high-boiling halide is placed in the bottom. When heated with an electric heating coil, the material boils and condenses on the sides of the tube. The height of the hot vapor is regulated by the rate of heating.

Low-temperature Thermostats.—Solid carbon dioxide ("dry ice") at −78°C. and liquid air at −180°C. furnish the simplest means of achieving low temperatures. Pieces of dry ice dropped slowly into acetone or "cellosolve" in a vacuum bottle give a liquid bath at about −78°C.

Liquid ammonia poured out of an inverted ammonia tank into a vacuum bottle gives a constant temperature bath at −39°.

Commercial refrigerating units are convenient for temperatures not too far below 0°C.

A volatile liquid such as acetone in a vacuum bottle can be operated as a thermostat by bubbling air through at such a rate that the cooling from evaporation just offsets the warming from the room.

A liquid can be thermostated at a low temperature by adjusting the depth to which a cold tube containing dry ice is immersed, and carrying out controlled additions of electrical heat. The rate of cooling can be adjusted also

[1] SMITH, *Ind. Eng. Chem.*, **16**, 22 (1924); RAMSPERGER and WADDINGTON, *J. Am. Chem. Soc.*, **55**, 214 (1933).

by changing the pressure of gas between an inner and an outer wall of a glass vessel.

By proper choice of liquids with suitable freezing points it is possible to make constant-temperature baths at several different temperatures.[1] Thus when dry ice in sufficient quantity is added to ethylene glycol in a vacuum bottle and stirred, a mush is produced which remains at 15° for several hours.

Convenient mixtures with solid carbon dioxide and their constant temperatures are as follows:

Ethylene glycol	−15°C.
Diethylene glycol	−31*
Dimethoxytetraethylene	−37
Diethyl carbitol	−54
Carbitol acetate	−67
Cellosolve	−77

Liquid air and liquid hydrogen[2] are used for low temperatures.

Salt Thermostats.—Salt cryohydrates are used to obtain temperatures between 0 and −50°C. These are prepared by freezing a solution of approximately the cryohydric concentration; then either ice or salt will separate until the cryohydrate point is reached, at which point the temperature becomes constant. Cryohydrates commonly used are given below.

	Degrees Centigrade		Degrees Centigrade
$CaCl_2 \cdot 6H_2O$	−54.9	$ZnSO_4 \cdot 7H_2O$	−6.6
$MgCl_2 \cdot 12H_2O$	−33.6	KNO_3	−2.9
$NaCl$	−21.1	$FeSO_4 \cdot 7H_2O$	−1.82
NH_4NO_3	−17.4	$Na_2SO_4 \cdot 10H_2O$	−1.2
KCl	−11.1		

The transition temperature of a salt is used to obtain a constant temperature in a manner exactly analogous to the use of a melting solid. The following transition temperatures, compared with the hydrogen scale, are among the more definitely known. They have been determined by Richards and his coworkers.[3]

	Degrees Centigrade
$Na_2CrO_4 \cdot 6H_2O$	25.90
$Na_2SO_4 \cdot 10H_2O$	32.383
$Na_2S_2O_3 \cdot 5H_2O$	48.0
$NaBr \cdot 2H_2O$	50.674
$MnCl_2 \cdot 4H_2O$	58.089
$Na_3PO_4 \cdot 12H_2O$	73.4

[1] WIKOFF, COHEN, and GROSSMAN, *Ind. Eng. Chem. Anal. Ed.*, **12**, 92 (1940).

[2] KEYES, *et al.*, *J. Am. Chem. Soc.*, **59**, 1426 (1937).

[3] RICHARDS, *et al.*, *Z. physik. Chem.*, **28**, 313 (1899); **43**, 465 (1903); **56**, 348 (1906); **61**, 313 (1907); *J. Am. Chem. Soc.*, **33**, 847 (1911).

CHAPTER XXX

THERMOMETERS AND THEIR CALIBRATION[1,2]

Mercury Thermometers

The mercury thermometer is the simplest and most widely used instrument for measuring temperature. Mercury is particularly suitable because it has a very uniform coefficient of expansion, it does not wet glass, it is easily purified, and the thermometer is easily read. At atmospheric pressure it remains liquid from -40 to $+360°C$.

Thermometers of various grades and ranges are available, including: (a) 0 to 360°, graduated in degrees for general purposes; (b) 0 to 50° and 50 to 100°, graduated to 0.1° for more accurate measurements; (c) 18 or 20 to 25°, graduated to 0.01° for calorimetric work; and (d) sets of thermometers from -40 to $+400°$, each having a range of 50° and graduated to 0.1°.

The graduations should extend a little beyond these limits, and a high-grade thermometer of any range should have an ice point for standardization. The thermometer is usually used in a vertical position.

Reading.—Exposed stem, parallax, and sticking mercury constitute three important errors in reading thermometers.

Thermometers are usually calibrated for total immersion of the mercury, and a correction is necessary when part of the stem is exposed. The thermometer will read too low if the air surrounding the stem is colder than the bath in which the bulb is immersed, and too high if the air is warmer. A second thermometer is placed near the exposed stem, and the stem correction S is given by the formula

$$S = 0.00016n(t' - t)$$

where n = the length of exposed mercury column in terms of scale degrees.
   t' = the temperature of bath.
   t = the average temperature of emergent stem.
The factor 0.00016 is suitable for the glass used in most thermometers.

It should be emphasized that stem corrections are not accurate, and for very high or very low temperatures a considerable error may be introduced. It is better to avoid the exposed stem by improving the experimental conditions.

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[1] A complete reference book on this subject is "Temperature, Its Measurement and Control in Science and Industry," Reinhold Publishing Corporation, New York (1941). It includes 125 papers presented at a symposium.

[2] Full details for calibrating thermometers are given by REILLY, RAE, and WHEELER, "Physico-chemical Methods," pp. 347 to 395, D. Van Nostrand Company, New York (1939).

Parallax may cause an erroneous reading, depending on the extent to which the eye is below or above the level of the top of the mercury thread. It may be eliminated completely by reading the thermometer from a distance with a cathetometer (telescope and cross hair), and it may be reduced considerably by carefully regulating the position of the eye. Special thermometer lenses sliding along the stem are helpful.

A thermometer should be read whenever possible with a rising thread rather than a falling thread, and it is necessary in accurate work to tap the thermometer gently before reading to prevent sticking.

Standardization.—In the simplest method, the thermometer is compared with a standard thermometer, for which purpose a thermometer standardized at the Bureau of Standards is useful. The two thermometers are set side by side in a thermostat, vapor bath, or large well-stirred body of liquid. The Bureau of Standards thermometer is immersed nearly to the top of the thread, and the other thermometer is immersed to the depth at which it is to be used. The true temperature as given by the standard thermometer is obtained by adding or subtracting the correction indicated on the Bureau of Standards certificate. A positive correction is to be added and a negative correction is to be subtracted.

An illustration of the correction is given below. A standardized thermometer wholly immersed in the vapor of a boiling liquid registered 80.05°, and the Bureau of Standards correction was −0.02°. The correct temperature of the vapor was then 80.03°. A second thermometer, under the same conditions, gave a reading of 79.91°. The second thermometer read too low by 0.12° and, therefore, 0.12° should be added to any temperature in the region of 80° read on this particular thermometer.

The ice point is always taken before a standardization, and it should check with the ice point given on the certificate, if the corrections as given in the certificate are to apply. In case the ice point does not check, a constant correction to all the corrections is necessary. For example, in the thermometer described above, the ice point was −0.01°. If after long aging the ice point should read −0.02° instead of −0.01°, all the corrections given in the table would also be too low by 0.01° and each should have 0.01° added.

In taking the ice point of a thermometer, it is necessary to have the ice very finely divided and intimately distributed throughout the whole bath. A large layer of water is not allowed to accumulate, and the spaces between the pieces of ice must be filled with water—not air. For ordinary work, finely shaved, close-packed ice in distilled water makes a satisfactory ice bath. For precision work, the recommendations of White should be followed (page 78).

Fixed boiling points, freezing points, or transition temperatures of pure materials are also used for standardizing thermometers (pages 419 to 420).

Beckmann Thermometer.—A Beckmann thermometer is shown in Fig. 108. This instrument reads directly to 0.01°, and can be estimated to 0.001°. Its range is only 5 or 6°, but it can be set for any temperature by adjusting the mercury in the reservoir at the top of the scale. The thermometer is warmed until sufficient mercury has been driven over into the reservoir, and it is then

given a sharp tap with the hand to break the thread at the entrance to the reservoir.

The thread is broken when the temperature is a little above the desired temperature, because a certain amount of cooling is necessary to bring the mercury back on the scale.

If the mercury is below the scale, mercury must be brought in from the reservoir at the top. The thermometer is warmed until mercury flows into the reservoir, and it is inverted so that the mercury connects with the mercury in the reservoir. The thermometer is then turned back into an upright position, very cautiously, and allowed to cool slowly. When the mercury is a little above the desired temperature, the thread is broken as before with a sharp tap. The flow of mercury through the long tube is slow, and time must be given to come to equilibrium before breaking the thread. In some thermometers an auxiliary scale is provided for the reservoir to assist in rapid setting.

Other Liquid Thermometers.—If thallium is added to the mercury to give an 8.5 per cent solution, the amalgam will go to $-60°$ before freezing. Liquid pentane can be used down to liquid-air temperatures, and toluene can be used to $-100°$, which is below the carbon dioxide–snow temperature. Alcohol is not used for high-grade thermometers because its thermal expansion is not uniform at all temperatures.

Fig. 108. Beckmann thermometer.

Gas Thermometers

Gas thermometers are not often used in ordinary work because they are less convenient than other types. In one of the simplest types, two bulbs filled with air are connected through a sulfuric acid manometer. One bulb is used as the thermometer and the other is placed in an ice bath. The pressure is adjusted by running out mercury from a reservoir and weighing it. Details of manipulation are given by Callendar.[1]

Resistance Thermometers

The electrical resistance of a wire increases in a regular manner as the temperature rises, and, since the resistance of a wire can be measured with great precision, this measurement offers an accurate method for determining temperatures.

Platinum wire is usually used because of its chemical inertness and its high resistance. It must be of the highest grade, carefully purified, and annealed by heating to redness with an electric current. It is annealed again at a lower temperature after winding.

The wire is wound on a frame, usually of mica, set into a long tube of glass, quartz, or porcelain and protected with a moisture-tight seal of de Khotinsky

[1] CALLENDAR, *Proc. Roy. Soc., London*, **50**, 247 (1891).

cement or other material.   The lead wires of copper or gold are connected to one arm of a Wheatstone bridge, and the second arm of the Wheatstone bridge contains a variable resistance in series with leads similar to those of the thermometer coil.   This second pair of leads is short-circuited inside the thermometer and is so arranged that the resistance of the leads is canceled out. Slight electromotive forces of a thermal nature are detected and canceled out by reversing the current through the bridge.   If there is no thermoelectric disturbance, the two readings will be the same; if there is a difference in the two readings, an average value is taken.

Other types of leads and bridges are described by Dickinson and Mueller[1] and by manufacturers.[2]

For calorimetric work, it is necessary to have the resistance wire in close thermal contact with the surroundings for quick readings.   The wire is wound around a narrow strip of mica and insulated with two thin sheets of mica. The whole is slipped into a sheath of silver made by arc welding, and the sheath is then soldered to a long glass tube, which terminates in a head provided with binding posts.   Full directions for construction are given by Dickinson and Mueller.[1]   In tubes of pyrex glass or quartz, the thermometers can be used at high temperatures.

The platinum-resistance temperatures t_p are given by the simple formula

$$t_p = \frac{R_t -}{R_{100} -} \cdot 100$$

where R_0 and R_{100} are the resistances of the platinum thermometer at $0°$ and $100°$.   This simple formula is not exact, and a second formula is necessary to convert these readings to the international scale.

$$T - t_p \qquad \left(\frac{T}{100} - 1 \right) \frac{T}{100}$$

T is the absolute temperature and δ is a constant which must be determined experimentally, using ice, steam, and boiling sulfur vapor.   The value of δ depends on the purity of the platinum and should not be greater than 1.52.[3]

A resistance thermometer using copper wire is accurate and easily made.[4]

Thermocouples

In a closed circuit of dissimilar metals, a current is generated when the junctions are at different temperatures.   A simple thermocouple or thermel is shown in Fig. 109, together with a multiple-junction thermel.   The heavy line represents one metal, and the lighter line represents the other.

[1] DICKINSON and MUELLER, *Phys. Rev.*, **24**, 529 (1907); *Bur. Standards Bull.*, **9**, 483 (1913).

[2] "Resistance Thermometers," Leeds & Northrup Company, Philadelphia.

[3] International Critical Tables, vol. I, p. 54, McGraw-Hill Book Company, Inc., New York (1926).

[4] MAIER, *J. Phys. Chem.*, **34**, 2860 (1930).

Various pairs of metals may be used. Copper-constantan is most often used in calorimetry and from room temperatures up to 350 or 400°. From 400 to 1000°, base-metal alloys are usually employed; for high temperatures, platinum with platinum containing 10 per cent rhodium or iridium is necessary.

A copper-constantan thermocouple gives an electromotive force of about 0.04 millivolt per junction per degree centigrade. It is somewhat larger than that of the other pairs. The junctions are so arranged that the copper terminals are on the outside and lead to the galvanometer, because new thermal junctions would be set up if the constantan wire were attached to the copper or brass binding posts.
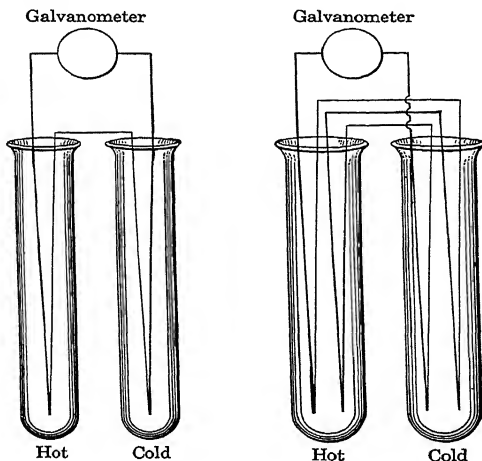
Fig. 109.—Thermocouples.

Copper and constantan[1] may be soldered together by using rosin or other noncorrosive flux, but the other metals are welded together in an oxygen-gas flame or in an electric arc. The two wires are twisted together for a short distance, held in an insulated clamp, and connected to one pole of the electric circuit (110 volts). An insulated carbon rod is connected through a suitable resistance (15 ohms) to the other electrode. The rod is touched to the end of the thermocouple and pulled away slightly, giving an electric arc. As soon as the two wires are welded together, the electrode is pulled farther away to stop the arc.

For room temperatures the cloth or enamel insulation is sufficient, but at high temperatures the wires are carefully insulated with porcelain tubes. It is essential to protect the thermels from corrosion; in furnaces, long gas-tight

[1] Constantan wire may be purchased under the trade name "Ideal" from chemical dealers or from the Driver-Harris Wire Co., Newark, N. J.

tubes of glass, porcelain, or quartz are used. In working with solutions at room temperatures, the thermel is usually encased in a thin glass tube, frequently filled with oil to give better thermal contact. When several junctions are used, the exposed junctions come at higher and higher levels in the encasing tube to prevent short-circuiting.

For precision work, the wire must be carefully selected and tested. Full particulars for making and using these thermoelectric thermometers are given by White[1] and by Adams.[2] They can be made sensitive to 0.00001°.

A thermoelectric thermometer is used either with a potentiometer (page 371) or with a millivoltmeter or galvanometer. The former is necessary in precision work, but the latter is so much more convenient that it is used in industrial work.

In the latter case, the current is measured rather than the electromotive force, and an error is introduced because the change in current with temperature is due not only to the thermel electromotive force but also to the change in resistance of the wires. To minimize this error, large wires are used so that the changeable resistance of the thermel is small in comparison with the fixed resistance of the galvanometer.

Galvanometer or millivoltmeter scales may be calibrated directly in terms of degrees. The resistance of the thermel should be about equal to the critical damping resistance of the galvanometer.

Thermocouples are used extensively in many industrial operations.[3] Recording instruments are made in which the galvanometer needle carries a pen and is pressed down against a moving drum of paper at intervals by a clock mechanism.

For accurate work, the potentiometer is specially designed to avoid spurious thermal electromotive forces or leakage. Reversing switches are particularly useful in this work. The White potentiometer is undoubtedly the best instrument for use with thermocouples.

The cold junction is usually set into cracked ice in a vacuum-jacketed bottle, but in crude work at high temperatures it is sometimes left at room temperature. A fluctuation in the temperature of the cold end is, of course, just as effective as a fluctuation in the furnace; the temperature read is the difference in temperature between the two junctions.

Thermocouples are calibrated with fixed temperatures, of which the most common are melting ice, 0.0°; boiling water, 100° (barometer correction); the transition temperature of sodium sulfate, 32.383°; boiling sulfur, 444.6°; melting lead, cadmium, tin, zinc, gold, and palladium (pages 148 and 189).

Alumel-chromel thermocouples are convenient for higher temperatures. The temperature equivalent of the voltage is found in tables.[4]

[1] WHITE, *J. Am. Chem. Soc.*, **36**, 2292 (1914).

[2] ADAMS, *J. Am. Chem. Soc.*, **37**, 481 (1915); International Critical Tables, vol. I, p. 57, McGraw-Hill Book Company, Inc., New York (1926).

[3] Catalog E, Hoskins Manufacturing Co., Detroit; International Critical Tables, vol. I, p. 59, McGraw-Hill Book Company, Inc., New York (1926).

[4] "Thermocouples, Assemblies, Parts and Accessories," Leeds & Northrup Company, Philadelphia (1940).

Optical Pyrometers

Optical pyrometers depend on the fact that the radiation emitted by a hot body is a function of the temperature. They are very easy to use, and are popular in industrial control operations. They are about the only instruments that can be used for very high temperatures. They are not suitable for temperatures below 500 or 600°, because the radiation is not sufficiently intense.

Several types are available, but the disappearing-filament type shown in Fig. 110 is one of the simplest and most practical.

The furnace, crucible, or other hot object is viewed through the telescope. An electric-light bulb with a carbon filament is placed in the optical system so that the observer sees the filament across the field. A variable resistance changes the current through the lamp. The wire appears bright on a darker
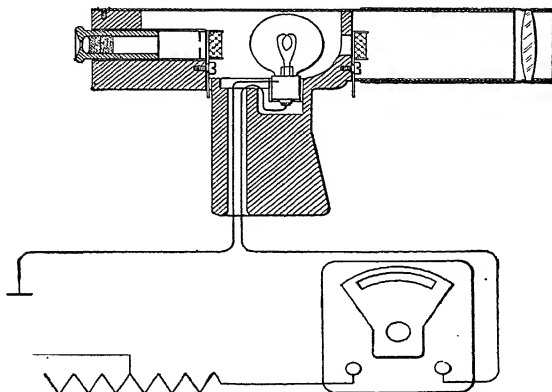
Fig. 110. —Radiation pyrometer of the disappearing-filament type.

field when the wire is hotter, and it appears dark on a light field when it is colder. When the two temperatures are exactly the same, the filament disappears and the whole field becomes uniform. A red screen is used, and for very high temperatures the brightness of the radiation from the furnace is brought down with a thicker screen. The current required to make the filament disappear is noted on the milliammeter, and the corresponding temperature is obtained by reference to a table supplied by the manufacturers for use with the lamp.

The table is prepared by calibrating the lamp at known temperatures, reading the milliammeter when the rheostat is so adjusted as to make the filament disappear. A few readings are sufficient, the rest being obtained by interpolation. The temperature of the furnace may be determined with a thermocouple, or the furnace may be gradually heated until a strip of pure metal melts and breaks an electrical circuit. The melting points of lead,

tin, zinc, silver, gold, osmium, or other metals may be used for calibration temperatures.

The furnace should be nearly closed and viewed through a small opening so as to give true black-body radiation.   If an open strip of metal is viewed, the calculated temperature may be considerably too low.   Empirical corrections for platinum and various other metals have been worked out.   A full description of optical pyrometers of this type, and others, is given in books on pyrometry.[1,2,3]

[1] "Optical Pyrometers," Leeds & Northrup Company, Philadelphia.

[2] FORSYTHE, *Bull.* 153, *Supp., Am. Inst. Mining Met. Eng.,* p. 2547 (1919).

[3] An excellent description of thermocouples and optical pyrometers is given by FOOTE, FAIRCHILD, and HARRISON, Pyrometric Practice, *Bur. Standards Tech. Paper* 170 (1921).

CHAPTER XXXI

VACUUM TUBES

The three-element vacuum tube consists of a filament, a plate electrode, and a grid electrode in a highly evacuated glass bulb which is fitted with suitable connecting posts. The connecting posts fit into standard sockets.

The filament consists of a loop of tungsten wire, sometimes coated with thoria, which, when heated to redness by means of an electric current, serves as a source of electrons and is, therefore, the cathode. The electrons are drawn across the tube by means of a positive potential placed upon the plate electrode or anode. The number of electrons which pass the evacuated space, and, therefore, the space current, depends upon the magnitude of the positive potential applied to the plate, provided that the temperature of the filament is
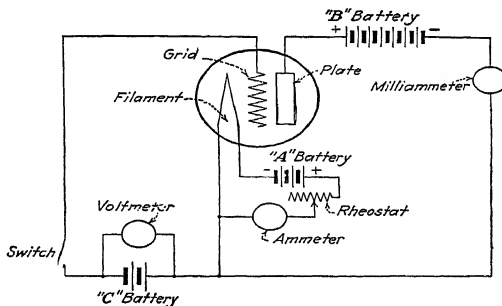
Fig. 111.—Circuit for determining characteristics of vacuum tubes.

maintained constant. The instrument described to this point corresponds to the older "Fleming valve."

If the third element, the grid electrode, is introduced into the tube, the ease with which the space current can be controlled is greatly increased. If a positive potential is placed on the grid as well as on the plate, the electrons pass to the plate in greater numbers; if a negative potential is placed on the grid, electrons will be repelled and their flow across the tube will be retarded, lowering the space current. If a changing potential is applied to the grid, these changes will be indicated instantaneously in the space current. It is also found that the change in current produced by a relatively small change of grid potential requires a considerable change in the plate potential to produce an equal effect.

Before using a vacuum tube for any purpose, its characteristic curves should be determined. These curves ensure the most efficient use of the tube. The apparatus necessary to determine the characteristic curves of a tube is indicated in Fig. 111. The static characteristics are the values obtained with d-c potentials applied to the tube electrodes. Plate characteristic curves and mutual characteristic curves both give information of value. The plate characteristic curves are obtained by varying plate voltage and measuring the plate currents for different controlled grid-bias voltages, whereas the
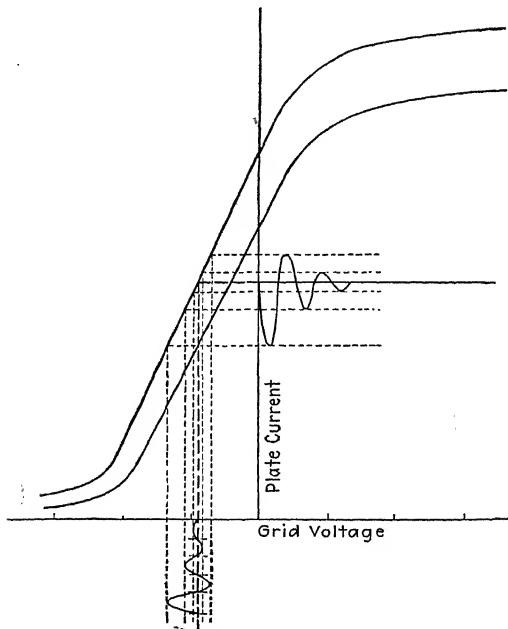
FIG. 112.—Operating characteristics of vacuum-tube amplifier.

mutual characteristic curves are the result of varying the grid-bias voltages and measuring the plate currents for different plate voltages. The operation of a tube can be described from these two families of curves.

Uses of Vacuum Tubes.—The number of individual applications of vacuum tubes to the work of a physical-chemistry laboratory is so great that complete description of all in this book is out of the question; however, a suggestion can be given of the kind of uses to which they may be put. Any tube containing three (or more) elements can be connected to function as (1) amplifier, (2) detector or rectifier, (3) oscillator or generator. The operations may take

place over a wide range of frequency, and many involve the use of different and complicated circuits, but the general principles of operation for the three purposes remain unchanged. After a brief description of these principles, certain of the specific uses will be enumerated.

1. *Amplifier.*—The mutual characteristic curves for a vacuum tube (grid potential *vs.* plate current) indicate that a small change in grid potential
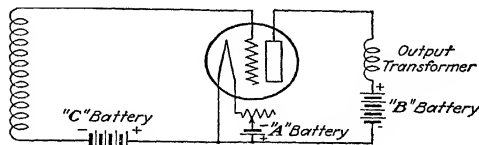
Fig. 113.—Vacuum tube in typical amplifier circuit.

makes quite a large change in plate current. Thus it is possible to apply voltages of any frequency to the grid, and to use the effect of the varying plate current in a coupling device to produce greater voltages and currents at the same frequency. Thus, the function of the grid is to control the power taken from the plate or B batteries. To give undistorted amplification, the tube must be adjusted to the circuit, by means of grid-bias potential, so that it operates on the straight portion of its characteristic curve. The operation of an amplifier can be understood from Fig. 112. One mode of connecting the tube in a typical amplifier circuit is shown in Fig. 113.

2. *Detector.*—A vacuum tube can function as a detector by adjusting it to operate on a bend in the grid voltage-plate current curve, rather than on the straight portion, as was the case for use as an amplifier. The principle upon which the operation as detector is based will be evident from Fig. 114, where, as indicated, the decrease in plate current when the grid is negative will be greater than the increase in plate current when the grid is positive. For

Fig. 114.—Operating characteristics of a vacuum-tube detector.

the sake of energy efficiency, detection is usually caused to take place on the lower bend of the curve by using a C battery to put a negative bias on the grid of the tube. Figure 115 illustrates operation on the lower bend of the curve; at the same time it shows how an oncoming electrical wave can be rectified. A typical detector circuit is shown in Fig. 116. Another commonly used detector circuit makes use of a grid leak and condenser in place of the grid bias.

3. *Oscillator.*—A third important function of a vacuum tube is to generate a continuously alternating voltage. Many different circuits have been employed, but they all depend on feeding more energy from the plate (or output) circuit to the grid (or input) circuit than is required to equal the power loss in the vacuum tube, using either capacitative or inductive coupling for this purpose. When a feeding back of energy occurs, the process is referred to
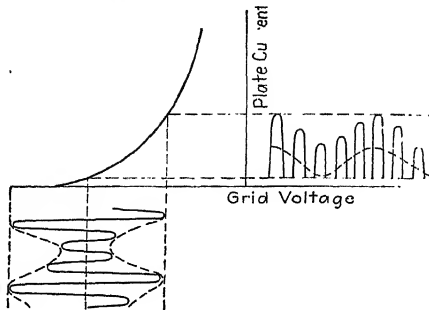
Fig. 115.—Operating characteristics of a tube detector with negative grid bias.

as regeneration; when the generation is sufficient, an oscillation results. The action consists of regular surges of power between the plate and the grid circuit at a frequency dependent on the circuit constants of inductance and capacity. By a proper choice of inductance and capacity, the frequency may be adjusted over very wide limits. For efficient operation at very high or very low frequencies, special types of circuit and special construction are used.
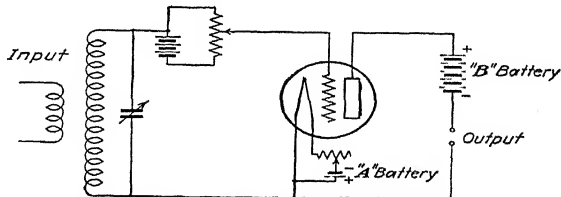
G. 116.—Vacuum tube in typical detector circuit.

A diagram showing the connections for an efficient oscillator for all ordinary frequencies accompanies this section (Fig. 117).

Laboratory Applications.[1]—Vacuum tubes serve for amplification purposes in experiments where the balance point of a bridge is involved. The accuracy of conductivity measurements can be increased greatly by the use of two or three stages of amplification in the detection of the signals. Both Jones and

[1] A complete description of vacuum tubes and circuits for laboratory work is now available: Mueller, Garman, and Droz, "Experimental Electronics," Prentice-Hall, Inc., New York (1941).

Josephs[1] and Shedlovsky[2] mention the use of vacuum-tube amplifiers in their valuable and comprehensive studies of the various sources of electrical error in bridge measurements. In accurate measurements of capacity for the subsequent calculation of dielectric constants, these methods of amplification of the signals are necessary. This is true for bridge, resonance, and heterodyne-beat types of apparatus. References to the literature are given at the conclusion of Exp. 62 and 63.

Employing a photoelectric cell with amplified current to operate a relay, Jones and Talley[3] have described an excellent method for the automatic registration of time.

Still another important application of the amplifier principle to laboratory use is found in the potentiometric-titration apparatus, in which the vacuum tube functions as a direct-current voltmeter. A review of potentiometric titrations by Furman[4] contains many references to work of this kind. Simple
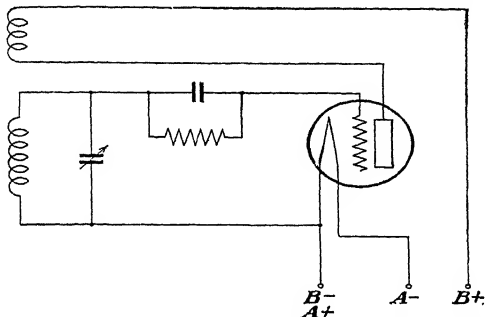
Fig. 117.—Oscillator with inductive feed-back coupling.

and direct-reading colorimetric circuits which involve the use of a photoelectric cell and single vacuum tube are available.[5]

One of the important applications of the vacuum tube from the standpoint of laboratory measurements is its use as an a-c voltmeter, in which case the tube functions as a detector. For use with potentials of a few hundredths to several volts, such a device has the advantage that it consumes practically no power. In addition, it responds with extreme rapidity, therefore it may be operated at high as well as low frequencies. The action of the tube as voltmeter, evident from the circuit diagram shown in Fig. 118, will be recognized as essentially that of a detector. The grid bias is adjusted for operation in the region of upward curvature of the characteristic curve.

[1] JONES and JOSEPHS, *J. Am. Chem. Soc.*, **50**, 1049 (1928).

[2] SHEDLOVSKY, *ibid.*, **52**, 1793 (1930).

[3] JONES and TALLEY, *J. Am. Chem. Soc.*, **55**, 624 (1933).

[4] FURMAN, *Ind. Eng. Chem. Anal. Ed.*, **2**, 213 (1930).

[5] PARTRIDGE, *Ind. Eng. Chem. Anal. Ed.*, **2**, 207 (1930).

The vacuum tube may serve as detector in the heterodyning of two oscillating circuits, for example, when this method is used for capacity determinations.

There have been described in the literature a large number of vacuum-tube oscillators for use in the bridge methods for the measurement of conductivity and capacity, and in the heterodyne-beat and resonance methods for the determination of capacity. The articles are now so numerous that it is not necessary to do more than refer to the sections of this manual which describe the technique of conductivity and capacity measurements where ample citations are given.

It is obviously beyond the scope of the present discussion to catalogue the large number of tubes that are now available. It will suffice to say that for
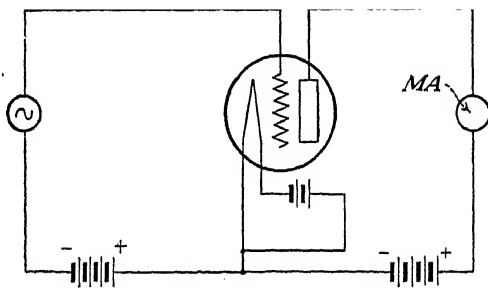
FIG. 118.—Vacuum tube as a-c voltmeter.

the different purposes enumerated there are special tubes designed to give the greatest efficiency. Also, in order to avoid some of the difficulties inherent in the three-electrode tube, bulbs containing four and five electrodes (supplementary grids) have come into common use. Present-day tubes are frequently of the heater type, *i.e.*, they make use of alternating current rather than direct current to evaporate electrons from the filament. This is convenient, because inexpensive transformers connected to the 110-volt a-c lighting circuit can furnish the required power. The newer tubes and improved circuits permit the elimination of B batteries, with the energy also being taken from a transformer. This is not always desirable for very accurate physical-chemical work.

CHAPTER XXXII

GLASS BLOWING

Every student is advised to practice with glass until he can join tubes, make T tubes, and perform the simple operations of glass blowing. Personal help from one who can blow glass is best, but a good deal can be accomplished with good books[1,2] and at least 50 hr. of practice.

When two pieces of hot glass are joined, a lump is usually produced, and it is necessary to remove this by blowing out the joint. An expert makes a smooth joint all in one operation, but a beginner usually finds it necessary to blow out part of the joint at a time and then allow it to contract by its own surface tension, repeating the process several times.

A blast lamp is always used, and the glass must be hot enough to blow easily. Glass should be heated gradually in the blast lamp by holding first at a considerable distance from the flame, and the joint is never allowed to cool until it is finished. An unfinished joint is quite likely to crack when heated.

Glass is never blown while it is actually in the flame, for the glass may then be too hot and blow out. If it is blown immediately after removal from the flame, the thin pieces will enlarge most; but if it is allowed to cool for a short time, the thin places will cool off, and thicker places, which hold their heat longer, will be the ones to expand. The joints should be of uniform thickness throughout. After a little practice, the operator makes use of these principles unconsciously.

In addition to the blast lamp, a few additional tools are desirable. They include a sharp triangular file for cutting, a carbon rod with sharpened end for enlarging the ends of tubes, a long rubber tube of narrow diameter and thick walls for blowing, a supply of glass rods, and an oxygen tank for pyrex and quartz. A handle with four flexible brass strips is convenient for holding flasks.

The table should be covered with asbestos board. Fresh, new glass should be used, and it is important not to mix different kinds. A rod of lead glass is necessary for sealing in platinum wires.

Cutting Glass Tubes.—Small tubes and rods are easily cut by making a file scratch with a *sharp* file, placing the two thumbs toward each other on either side of the scratch, and breaking with the hands.

In the case of large tubes, a small point of heated glass is touched against one end of the file scratch and a crack is produced under the file scratch which

[1] FRARY, TAYLOR, and EDWARDS, "Laboratory Glass Blowing," McGraw-Hill Book Company, Inc., New York (1928).

[2] STRONG, "Procedures in Experimental Physics," Chap. I, Prentice-Hall, Inc., New York (1939).

extends for a short distance beyond. The crack is then led around the whole tube in short stages, 2 or 3 mm at a time, by touching the heated glass point to the tube just beyond the end of the crack.

The tube may be cracked more neatly and more quickly by wrapping nichrome or other heating wire around the tube over the file scratch. The wire is heated red hot with an electric current, using a suitable resistance in series.

Joining Tubes.—The ends of the two tubes are heated in a fairly large flame until quite soft, but not to the point where they collapse. One of the tubes is previously closed at the opposite end by sealing off or inserting a cork. The two heated ends are forced squarely against each other and blown out to give a small enlargement. The tubes are then pulled apart slightly to bring the small bulb down to the diameter of the tube, and the whole joint is again heated to the softening point and allowed to cool slowly for annealing. A deposit of soot from a smoky flame helps to give slower cooling. The success
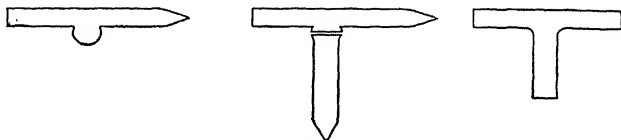
Fig. 119.—Making a T tube.

of the operation depends on having the glass sufficiently hot, placing the two ends exactly together, and pushing with the right force to give a temporarily slightly increased wall thickness.

In case inequalities in thickness remain, they must be removed before the joint cools off. The whole region is thickened by heating, and blown out, after cooling slightly to allow the thinner parts to solidify. Several localized heatings and blowings may be necessary for a beginner. If the inequalities have to be teased out in this unsatisfactory way by localized heating, it is especially necessary to heat the whole joint to the softening point for annealing.

If a capillary tube is to be joined to a tube of large diameter, one end of the capillary is heated until it is closed and a thick-walled bulb is blown out. The end of the bulb is then broken off or blown out in the flame, and the enlarged end thus formed is sealed to the larger tube.

Bulbs.—The chief difficulty in blowing bulbs is to get the glass walls thick enough. A tube is drawn down near one end and closed by fusing. The end is blown out to give a small bulb before the end becomes too thick, and the bulb is heated again until it contracts and thickens the wall. It is then blown out to the desired size. For a large bulb it is necessary to heat a considerable length of the stem, and several contractions and blowings may be necessary to give sufficient wall thickness.

T Tubes.—The operations of blowing a T tube are indicated in Fig. 119. A small flame is directed against the side of a closed tube, and a small bulb is

blown out. Just as soon as the spot becomes sensitive, it is blown out partially, and the flame is then directed against the enlargement. In this way, it is possible to avoid blowing a bulb of excessively large diameter. The end of the bulb is then broken off or blown out in the flame. The remaining walls should be thick, and they should project a short distance from the tube.

The second tube is then joined to the projecting walls in the manner shown. If inequalities in thickness remain, they must be removed by heating and blowing. The whole joint, including the entire circumference of the tube, is heated to the softening point for proper annealing. A rubber tube may be used so that the operator can see his work while blowing.

Sealing in Wires.—Wires are sealed in as shown in Fig. 120. A bead of glass is fused around the wire, and it is forced into a small hole blown in the tube while both the bead and the tube are hot. The whole joint is blown out and contracted by heating several times until smooth and uniform.

Platinum wire is necessary for most purposes, and a bead of lead glass must be used. Except with fine wire, ordinary glass will crack when cold if it

FIG. 120.—Sealing in a wire.

touches the platinum wire at any point. Dummet wire, a copper alloy, may be used for electrical connections through glass. Short lengths may be salvaged from discarded electric-light bulbs.

Glass to metal seals[1] usually involve the formation of a thin coating of metallic oxide which adheres firmly to the metal and at the same time dissolves in the glass. The coefficient of expansion of the glass and metal must be practically the same from the annealing temperature down to room temperature and any strain from thermal contraction must not exceed the tensile strength of the glass. An alloy of iron, cobalt, and nickel ("Covar") is used for sealing large tubes into special glass.

When tungsten wire is sealed into pyrex, the wire is first cleaned with fused sodium nitrite. It is then heated in the blast lamp to a peacock green, showing that the oxide coating is of just the right thickness. When the seal is finished, the glass around the seal should have a gold color. Platinum wire can be set into pyrex but it does not give a gastight seal.

Inner Joints.—A little more skill is required in blowing inner joints. The inner tube is flanged outward and the outer tube is flanged inward so that the two meet. The tubes are usually centered with small wedges of cork or asbestos, which can be removed later. The flanged edges are heated up slowly in a large flame, and then softened until they fuse together. If small holes are left, they may be plugged with the help of a narrow rod heated by the blast lamp. It may be necessary to blow out the joint and contract it several times. It must be annealed very carefully.

[1] HULL and BURGER, *Physics*, **5**, 384 (1934).

Quartz.—For blowing quartz, it is necessary to feed the blast lamp with compressed oxygen instead of air. Quartz blowing differs considerably from glass blowing, for the blowing must be done while the quartz is in the flame, and care must be exercised not to blow too hard and thus blow out the walls. The light is so intense that it is absolutely necessary to protect the eyes with dark glasses. Working with quartz has two advantages over working with glass, in that there is no danger of cracking from unequal cooling or heating and it is less necessary from a mechanical standpoint to remove all the inequalities in thickness. In fact, it is possible to put the joint under the water faucet to cool it more rapidly.

No metal can be sealed gastight into quartz, but electrodes may be ground into quartz vessels, or they may be sealed in with the help of graded seals. The graded seals, with quartz at one end and pyrex or soft glass at the other end, may be purchased, or they may be made up from several different glasses, each one in series having a lower silica content and slightly greater thermal expansion. Suggestions are given in "Laboratory Glass Blowing," by Frary, Taylor, and Edwards.[1]

Pyrex Glass.—Pyrex glass is largely used, particularly for work involving temperature changes. Pyrex requires a higher temperature to soften than does ordinary glass, and it is necessary to use a mixture of oxygen and air with the gas in the blast lamp. A simple T tube is used, and the oxygen supply is increased to give a flame of the proper temperature to soften the pyrex without too much melting.

Tungsten wires may be sealed into pyrex in the manner described for platinum in ordinary glass. The bead of pyrex glass on the tungsten wire should be worked in an oxidizing flame until the glass is slightly colored and a tight seal is ensured. Platinum wire does not make a gastight joint in pyrex.

Stopcocks.—Tight-fitting stopcocks of good workmanship are essential in accurate work. Stopcocks with an oblique bore are best, because with a straight bore a channel around the joint can give rise to a leak. A stiff grease is usually used, but in some cases where organic matter must be avoided the stopcock may be lubricated and rendered gastight with a syrup of phosphoric acid. When a small leak cannot be tolerated, a mercury-sealed stopcock is recommended. Several types are available, in which all joints are covered over with a layer of mercury.

Ground-glass joints are valuable for many pieces of apparatus. They are available now with interchangeable parts so that one joint may be fitted onto several different tubes or flasks.

[1] FRARY, TAYLOR, and EDWARDS, "Laboratory Glass Blowing," McGraw-Hill Book Company, Inc., New York (1928).

CHAPTER XXXIII

THE USE OF INDICATORS IN THE DETERMINATION OF HYDROGEN-ION CONCENTRATION

Given a series of suitable indicators and a series of buffer mixtures of progressively different pH values, the estimation of the pH value of an unknown solution by the use of indicators is readily possible. That indicator is suitable whose color in the unknown solution is intermediate between the color produced in more acid solutions and the color produced in more alkaline solutions. The buffer mixtures make it possible to determine the pH range over which the indicator changes color.

The action of most indicators may be explained by assuming that they are monobasic acids which show one color when ionized, and another when undissociated. The ionization may be represented by the equation

$$\text{Acid form} \rightleftarrows H^+ + \text{alkaline form}$$
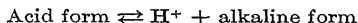
and, from the law of mass action,

$$\frac{a(\text{acid form})}{a(\text{alkaline form})}$$

or

$$pH = pK_a + \log \frac{}{1 - \alpha}$$

In this last equation the fraction α is the fraction of the indicator present in the alkaline form and $1 - \alpha$ is the fraction remaining in the acid form.

Each indicator has a definite pK_a and definite colors when completely in the alkaline and acid forms, and all gradations between these two extreme conditions have colors that represent the varying mixtures of these alkaline and acid forms. For the particular situation when fractions of alkaline and acid forms are identical, the pH of the indicator solution and the pK_A of the indicator are equal.

There are several systems that can be used in the determination of the pH of an unknown solution. Foremost among them are the color-standard buffer-solution procedure of Clark and Lubs[1] and the bicolor standard method without buffer of Gillespie.[2] In the bicolor system the pK_a value of the indicator must be known and the indicator must ionize as a weak monobasic acid.

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[1] CLARK, "The Determination of Hydrogen Ions," 3d ed., The Williams & Wilkins Company, Baltimore (1928).

[2] GILLESPIE, *J. Am. Chem. Soc.*, **42**, 742 (1920); "Physical Chemistry," McGraw-Hill Book Company, Inc., New York (1930).

In the Clark and Lubs procedure a series of buffer solutions of predetermined pH values is used to establish the pH value corresponding to each shade exhibited by the indicator in its color change. The effective range of an indicator is 1.6 pH units. To standardize the color change of the indicator 10 ml of buffer solution is placed in each of nine clear hard glass tubes with the pH values of the nine buffer solutions varying in intervals of 0.2 unit over the effective range. A definite amount of a standardized indicator solution is added with mixing to each of the tubes. With accurate preparation of such standards, color changes are exact and reproducible. The color standards are used to compare with test tubes that contain solutions of unknown pH value, made up in the same way with indicator solution. Since the color of indicators usually depends upon the ionic strength of the solution, the ionic strength of the buffers should all be alike, and, if possible, the same as that of the unknown.

Tables are included to give data for some indicators and a set of standard buffer solutions for pH values from 2.2 to 10.0 at 20°C. They have been selected for use by Clark and Lubs.

INDICATORS.   CLARK AND LUBS SYSTEM

Indicator	pK_a	pH range	Color change acid-alkali	Milliliters of alkali*
Bromphenol blue.......	4.0	3.0–4.6	Yellow-blue	14.9
Bromcresol green.......	4.7	3.8–5.4	Yellow-blue	14.3
Chlorphenol red........	6.0	4.8–6.4	Yellow-red	23.6
Bromcresol purple......	6.3	5.2–6.8	Yellow-purple	18.5
Bromthymol blue.......	7.0	6.0–7.6	Yellow-blue	16.0
Phenol red.............	7.9	6.8–8.4	Yellow-red	28.2
Cresol red.............	8.3	7.2–8.8	Yellow-red	26.2
Thymol blue...........	1.5 or 8.9	1.2–2.8 or 8.0–9.6	Red-yellow or yellow-blue	21.5

* The figures in this column indicate the volume of 0.01 M sodium hydroxide solution with which 0.1 g quantities of the respective dry indicators should be ground in a mortar and subsequently diluted to 250 ml to form a 0.04 per cent solution.

The bicolor system of Gillespie is based on the assumption that the change in color of the various indicators used is proportional to the degree of neutralization undergone by the indicator when it is considered as an acid. A double row of test tubes is placed in a rack; in one series of tubes is placed 10 ml of an acid solution and in the other series is placed 10 ml of an alkaline solution. One tube of acid solution and one tube of alkaline solution form a pair, and pairs of tubes take the place of buffers. Into each pair of tubes is placed 10 drops in all of the indicator, divided according to the following plan:

Alkaline tube receives.........	1	2	3	4	5	6	7	8	9
Acid tube receives.............	9	8	7	6	5	4	3	2	1
Corresponds to α =		0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9

STANDARD BUFFER SYSTEMS
pH Values 2.2 to 10.0 at 20°
Phthalate + HCl

pH	0.2M KH phthalate	0.2M HCl	Dilution
2.2	50 ml	46.60 ml	To 200 ml
2.4	50	39.60	200
2.6	50	33.00	200
2.8	50	26.50	200
3.0	50	20.40	200
3.2	50	14.80	200
3.4	50	9.95	200
3.6	50	6.00	200
3.8	50	2.65	200

Phthalate + NaOH

pH	0.2M KH phthalate	0.2M NaOH	Dilution
4.0	50 ml	0.40 ml	To 200 ml
4.2	50	3.65	200
4.4	50	7.35	200
4.6	50	12.00	200
4.8	50	17.50	200
5.0	50	23.65	200
5.2	50	29.75	200
5.4	50	35.25	200
5.6	50	39.70	200
5.8	50	43.10	200
6.0	50	45.40	200
6.2	50	47.00	200

KH$_2$PO$_4$ + NaOH

pH	0.2M KH$_2$PO$_4$	0.2M NaOH	Dilution
5.8	50 ml	3.66 ml	To 200 ml
6.0	50	5.64	200
6.2	50	8.55	200
6.4	50	12.60	200
6.6	50	17.74	200
6.8	50	23.60	200
7.0	50	29.54	200
7.2	50	34.90	200
7.4	50	39.34	200
7.6	50	42.74	200
7.8	50	45.17	200
8.0	50	46.85	200

Boric Acid + KCl + NaOH

pH	0.2M H$_3$BO$_3$ + 0.2M KCl*	0.2M NaOH	Dilution
7.8	50 ml	2.65 ml	To 200 ml
8.0	50	4.00	200
8.2	50	5.90	200
8.4	50	8.55	200
8.6	50	12.00	200
8.8	50	16.40	200
9.0	50	21.40	200
9.2	50	26.70	200
9.4	50	32.00	200
9.6	50	36.85	200
9.8	50	40.80	200
10.0	50	43.90	200

* This solution is prepared by dissolving 12.41 g of purified H$_3$BO$_3$ and 14.91 g of purified KCl in redistilled water and diluting to 1,000 ml.

If the resulting colors are viewed through each pair of tubes, the result will be the same as obtained in a solution to which 10 drops of an indicator have been added; if the color viewed through the pair of tubes thus described is compared to an equal depth of an unknown solution to which 10 drops of indicator solution have been added, a color match between the superimposed pair of tubes and the solution under examination can be obtained.

A table by Gillespie for pH values corresponding to various drop ratios for seven indicators is included for reference.

VALUES OF pH CORRESPONDING TO VARIOUS DROP RATIOS

Drop ratio alkali/acid	Brom-phenol blue	Methyl red	Brom-cresol purple	Brom-thymol blue	Phenol red	Cresol red	Thymol blue
1:9	3.1	4.1	5.3	6.2	6.8	7.2	7.9
2:8	3.5	4.4	5.7	6.5	7.1	7.5	8.2
3:7	3.7	4.6	5.9	6.7	7.3	7.7	8.4
4:6	3.9	4.8	6.1	6.9	7.5	7.9	8.6
5:5	4.1	5.0	6.3	7.1	7.7	8.1	8.8
6:4	4.3	5.2	6.5	7.3	7.9	8.3	9.0
7:3	4.5	5.4	6.7	7.5	8.1	8.5	9.2
8:2	4.7	5.6	6.9	7.7	8.3	8.7	9.4
9:1	5.0	5.9	7.2	8.1	8.6	9.1	9.7

The simplest device for making color comparisons is the block comparator. Where highest accuracy is necessary, spectrophotometers or special two-color colorimeters[1] may be used. Ordinary colorimeters cannot be used with two-color indicators.

and SNELL, "Colorimetric Methods of Analysis," D. Van Nostrand Company, Inc., New York (1936).

CHAPTER XXXIV

PURIFICATION OF MATERIALS

In many experiments, the limiting factor in accuracy is the purity of the materials rather than the refinement of the measurement. For example, nothing is gained by determining the refractive index of benzene to five decimal places if it contains enough thiophene to alter the refractive index in the third decimal place.

A considerable amount of technical knowledge and laboratory skill is necessary to purify materials sufficiently for precision measurements, and only a few general methods can be given here.

Methods.—The methods described by T. W. Richards in his atomic-weight researches offer the best means for purifying inorganic materials. His researches on the properties of organic liquids constitute excellent references in the latter field. A book by Weissberger and Proskauer[1] gives much valuable information concerning the purification of organic liquids and their physical constants.

Professor Timmermans,[2] of the University of Brussels, has studied very carefully the constants and purity of several organic liquids. The properties of these liquids have been critically evaluated, and the criteria of purity given. About 20 pure organic liquids have been prepared by Professor Timmermans under the authority of the Bureau International D'Étalons Physico-Chimique, and they may be procured in small quantities through the National Bureau of Standards.

Crystallization constitutes one of the best methods of purification. Several recrystallizations may be necessary. If a substance can be crystallized out in two different crystalline forms, a greater purity is ensured, for any impurity which might come out with the first crystals would be unlikely to crystallize out also in the second form.

Organic liquids are usually purified by distillation, and the boiling point (corrected to 760 mm) is one of the most common ways of giving an idea of their purity. If the boiling point changes during the distillation, the material is not pure, and only a small fraction of the distillate is used. On the other hand, a constant boiling point may be obtained with a constant-boiling mixture as well as with a pure liquid. The two may be distinguished by changing the pressure. The composition will be altered in the case of a constant-boiling mixture, but not in the case of a pure liquid.

[1] WEISSBERGER and PROSKAUER, "Organic Solvents," Clarendon Press, Oxford (1935).

[2] TIMMERMANS and MARTIN, *J. chim. phys.*, **23**, 733 (1926); **25**, 1 (1928).

One of the best criteria of purity is the constancy of the freezing point throughout the whole of the freezing process.[1] If the liquid is impure, the impurities will concentrate in the liquid phase as the solid separates out, and the freezing point will gradually decrease. If the last drop to solidify has the same freezing point as the first drop to solidify, the liquid is apt to be quite pure. A sensitive thermometer is needed.

Electrolysis is helpful in purifying metals that can be readily deposited electrolytically, such as silver, copper, zinc, thallium, and other metals. Another example of electrochemical purification is illustrated by adding zinc to a zinc chloride solution. All metals below zinc in the electromotive-force series are thrown out of solution by contact with the metallic zinc.

Drying is an important operation in purification. Salts crystallized from solution are quite likely to contain moisture, which is not fully removed until the crystal is fused. It may be necessary to fuse the salt in an atmosphere of some inert gas. If the material decomposes at a high temperature, it is heated for a longer time at a lower temperature, preferably while attached to a vacuum pump. Liquids can be dried by shaking with anhydrous calcium chloride, phosphorus pentoxide, or barium oxide. The liquid is then decanted and distilled.

Water.—Distilled water is sufficiently pure for most operations in physical chemistry, but for conductance experiments and certain others it is necessary to use specially prepared redistilled water.

Distilled water is boiled and a current of purified air is streamed through the condenser in the opposite direction. The air is first freed from carbon dioxide, ammonia, and other gases by passing through sodium hydroxide solution and then through sulfuric acid. Block tin or quartz is used for the condenser.

Purified water in small quantities may be prepared by redistilling distilled water from a flask containing potassium permanganate and a little sulfuric acid, and condensing in a block tin or quartz condenser. It is again redistilled after adding sodium hydroxide.

Mercury.—Mercury can be purified most easily by placing it in a bottle with concentrated sulfuric acid over it and bubbling air through for several days. Any possible danger from mercury poisoning is minimized by having the bottle nearly closed and drawing air through with a water aspirator.

The Hulett method[2] is recommended for preparing very pure mercury. In this method, shown in Fig. 121, the mercury is distilled under reduced pressure, while a slow stream of air is bubbled through to prevent bumping and to oxidize any basic metals present. A distilling flask of pyrex is drawn down at the neck and fused to a vertical pyrex tube 30 cm or more in length. A second tube is drawn down to a long capillary and inserted inside this larger tube, and the joint is made airtight with a rubber tube. Over the top of the

[1] WHITE, *J. Phys. Chem.*, **24**, 393 (1920): ANDREWS, KOLM, and JOHNSON, *J. Phys. Chem.*, **29**, 918 (1925).

[2] HULETT, *Phys. Rev.*, **33**, 307 (1911).

second tube is a short rubber tube and a screw cock. An extra pyrex tube is sealed on to the delivery tube, giving an air condenser 50 to 100 cm long. The open end of this passes through a rubber stopper into a filter flask, which is connected with a vacuum pump or aspirator. The screw cock is opened only far enough to permit occasional bubbling of air through the mercury. The flask is heated on a wire screen or sand bath with a Bunsen burner, and the flask may be covered with asbestos to prevent excessive condensation on its walls.

Alcohol.—Ethanol is treated with silver oxide to remove aldehydes, and distilled from calcium oxide (after long digestion) to remove water. Metallic calcium and metallic sodium are also effective in removing water, but they are less satisfactory because they produce alcoholates also. It is very diffi-
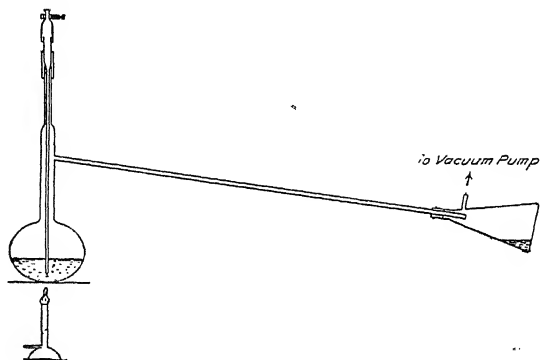
Fig. 121.—Purification of mercury.

cult to get the last trace of water out of ethanol, and the pure alcohol takes up moisture very quickly from the air.

Acetone.—Acetone can be purified effectively by crystallization with sodium iodide.[1] Sodium iodide is dissolved in hot acetone to give a nearly saturated solution. The solution is then cooled in ice, and the crystals of $NaI \cdot 2(CH_3)_2CO$ are filtered, dried, and heated to 50°C. in an oven. The crystals are then transferred to a flask and heated to distill off the acetone. The impurities present in acetone do not crystallize out with the sodium iodide.

Benzene.—Benzene may contain thiophene and other sulfur compounds which have about the same boiling point. It is necessary to remove them by chemical methods. The benzene is shaken thoroughly, preferably in a mechanical shaker, with concentrated sulfuric acid. It is poured off, rinsed with water, and shaken with mercury. If no black deposit is formed on the mercury, the benzene is free from sulfur compounds, and it is then dried and

[1] SHIPSEY and WERNER, *J. Chem. Soc.*, **103**, 1255 (1913).

purified by distillation, two or three fractional freezings (5.48°), and a final distillation.

Toluene and other aromatic hydrocarbons are purified in a similar manner. It is a good plan to let mercury stand in the bottom of a bottle of toluene for a year or more. Purified in this simple way, the toluene is suitable (after distillation) for use in thermoregulators.

Sodium Chloride.—Since sodium chloride has a small temperature coefficient of solubility, it cannot be easily purified by crystallization. A saturated solution of sodium chloride is treated with hydrochloric acid gas to throw out the pure salt. The hydrochloric acid gas is introduced through an inverted funnel because a small tube is soon plugged up with the crystals. Rubber connections are attacked by hydrochloric acid, and the connections and the generating bottle are all of glass. The gas is generated by dropping concentrated hydrochloric acid, drop by drop, into concentrated sulfuric acid while shaking to avoid the formation of two layers, which might lead to an explosion.

The precipitated sodium chloride is packed into a funnel, rinsed with a minimum amount of water, and fused in a platinum dish at red heat.

Sodium Hydroxide.—For most titrations with alkali, it is necessary to have the alkali free from carbonate to obtain a sharp end point. High-grade commercial sodium hydroxide may now be obtained which ordinarily needs no further purification. Sodium hydroxide solution free from carbonate is readily prepared from a saturated stock solution. The carbonate is thrown out as an insoluble precipitate by the high concentration of sodium hydroxide which exists in a saturated solution. The clear supernatant solution is drawn off with a siphon and diluted with carbon dioxide–free water to the desired concentration, at room temperature. The saturated solution is about $15M$, and it is kept in a bottle, the inside of which has been covered with paraffin.

The purification of other substances may be found in the literature. Inorganic substances have been discussed by Archibald.[1]

[1] ARCHIBALD, "The Preparation of Pure Inorganic Substances," John Wiley & Sons, Inc., New York (1932).

CHAPTER XXXV

ERRORS

Determination of Errors

An important part of any experiment in physical chemistry is the a
and computation of the experimental data and, along with them, the
tion of the reliability of the result. It is impossible for th   result of any
measurement to be mathematically exact.   ent or series of
measurements indicate there is a certain p   true magnitude
will lie within definite limits.   Errors are   as being either
systematic or observational in character.

1. Constant and Systematic Errors.—Included
due to weather conditions, to inherent defects in in
calibration against standard), and to prejudice.
or corrected by careful planning of experiments.

2. Observational Errors.—These errors are of   or causes
that lie beyond the control of observer.   The pres   ; made
evident by the discrepancies between ind.
quantity made apparently under identical
sources of disturbance have been removed.

The laws of probability are of great value in the treatment of observational
errors.   Thus, for any series of measurements of a given quantity they
is greater than the 1
errors of like magnit

$$y =$$

where y is the frequency of occurrence of a deviation of magnitude x, e is the
logarithmic base, and h is an abstract number sometimes taken as
cal estimate of the reliability of the observation known as
The constant h is given by the equation

where n is the number of observations and $\Sigma(d)$ is the sum of the deviations.

There are several convenient ways of expressing the accuracy of an experi-
mental result.   Average, mean, and probable errors are simply calculated and

related to one another. In chemical work the arithmetic mean of the results is coming into favor as the best or most practical value because measurements of a sufficiently high order of accuracy to justify any more elaborate treatment of the results are unusual.

1. Average Error.—The average error is simply the mean of the errors, and measures the average deviation of each observation from the mean of the whole series. The deviation of a single observation from the mean of the series is denoted by the symbol d. The average error depends upon the proportion in which the errors of different magnitudes occur, and upon the magnitude of the individual errors.

Average error of single observation:

$$a = \pm \frac{\Sigma(d)}{n}$$

Average error of result of n observations:

$$A = \quad \sqrt{n}$$

In these expressions, $\Sigma(d)$ denotes the sum of the absolute deviations ($\pm d$) of every observation from the mean or average value of the quantity.

2. Mean or Mean-square Error.—The mean error is defined as the error whose square is the mean of the squares of all the errors. It depends upon the principle of least squares, according to which the best value of an observation is that one which makes the sum of the squares of the deviations a minimum.

Mean error of single observation:

$$m = \pm$$

Mean error of result of n observations:

$$M = \pm \quad n(n - 1)$$

3. Probable Error.—The probable error determines the degree of confidence we may have in using the average as the best representative value of a series of observations. It is the error such that the number of errors greater than p, the probable error, is equal to the number of errors which are less than p.

Probable error of single observation:

$$p = \frac{0.4769}{} \quad \pm 0.6745 \quad \prime n - 1 \cong \pm 0.8453 \quad \sqrt{n(n - 1)}$$

Probable error of result of n observations:

$$\pm 0.6745 \sqrt{\frac{\Sigma(d^2)}{}} \cong 0.8453 \cdot \frac{\Sigma(+d)}{}$$

The approximation formulas avoid the necessity of having to square the residual errors in case a large number of observations have been made.

To illustrate the use of these equations we shall calculate average, mean, and probable errors for the radius of the bore of a certain capillary tube which has been used for the determination of the surface tension of liquids. Individual values reported are 0.02025, 0.02028, 0.02013, 0.02019, 0.02032, 0.02021 cm. The average value for the radius is 0.02023 cm.

a = average error of a single observation

$$= \pm \frac{}{n} = \pm \left(\frac{}{6} \right.$$

A = average error of mean result of the six observations

$$\frac{\Sigma (}{\sqrt{}}$$

m = mean error of single observation

$$\pm \sqrt{\frac{}{n-1}} = \pm \sqrt{\frac{+ 25 + 100 + \overline{16} + 81}{5}} \qquad \pm 0.000068$$

M = mean error of result of the six observations

$$\sqrt{\frac{230}{5 \times 5}} \cdot 10^{-5} = \pm 0.000027$$

p = probable error of single observation
$$= \pm 0.675 m = \pm 0.000045$$
P = probable error of result of the six observations
$$= \pm 0.675 M = \pm 0.000018$$

Influence of Errors of Observation on the Final Result

A final physical-chemical result is usually obtained by combining the results of different kinds of measurements. The accuracy of any final result is influenced by the accuracy of the measurements of the several quantities involved. If it happens that one of the quantities involved is subject to a much greater error than the others, it will have the preponderant effect in determining the accuracy of the final result, otherwise the errors must be combined in specific ways. There are a number of rules which are convenient in combining measurements affected with different mean or probable errors. The following formulas, describing the probable error where sums, differences, products, quotients, and proportions are involved, are useful.

1. The probable error of the sum or difference of two quantities A and B, respectively, affected with probable errors $\pm a$ and $\pm b$, is

$$P = \pm \sqrt{a^2 + b^2}$$

2. The probable error of the product of the two quantities A and B is

If a third mean, C, with probable error $\pm c$, is included,

$$P = \pm \sqrt{(BCa)^2 + (ACb)^2 + (ABc)^2}$$

3. The probable error of the quotient (B/A) of the two quantities A and B is

$$P = \pm$$

4. The probable error of the proportion $A/B = C/x$ is

$$P = \pm \frac{+ \qquad + (Bc)^2}{A}$$

Significant Figures

The accuracy of a measurement is often indicated by the number of significant figures used in recording its magnitude, and care must be exercised that too many significant figures are not used.   Enough significant figures are retained so that the uncertainty in the next to the last figure is not greater than unity.   Thus, if one reads exactly 25° on a thermometer graduated in degrees, the observation will be recorded as 25.0 because the figure 5 is certain and tenths of a degree can be estimated.

In addition and subtraction every figure is dropped which falls under an unknown digit in any of the quantities involved, whereas in multiplication and division the final result should retain only as many significant figures as there are in the factor containing the smallest number of significant figures. Most of the multiplications and divisions required for the work of a physical-chemistry laboratory course may be made with advantage with four-place logarithm tables or good slide rules.

In general, the accuracy with which the least accurately observable quantity can be measured limits the precision of the final result and so determines the accuracy with which an experimenter seeks to measure the other quantities involved.   If a measured quantity enters once into an equation as a term that is to be raised to a power higher than one, it must be determined with a correspondingly greater precision, but it will be noted that in the case of the computation of molar refractivities by the formula of Lorentz and Lorenz, the square of the refractive index appears twice in such a manner that the accuracy of the computation is really limited by the precision with which the density can be observed.   Such considerations show that all but the simplest of equations require applications of error theory for intelligent procedure.

A more complete discussion of errors in chemical operations has recently become available.[1]

[1] CRUMPLER and YOE, "Chemical Computations and Errors," John Wiley & Sons, Inc., New York (1940).

APPENDIX

Reduction of Barometer Readings on a Brass Scale to 0°

$$b_0 = \frac{1 + \beta t}{1 + \alpha t}\, b = \left(1 - t\,\frac{\alpha - \beta}{1 + \alpha t}\right) b$$

b = observed barometer reading.
t = temperature of the barometer.
$\alpha = 0.0001818$ = mean cubical coefficient of expansion of mercury between 0 and 35°.
$\beta = 0.0000184$ = linear coefficient of expansion of brass.
b_0 = barometer reading reduced to 0°.

Corrections to Barometer Readings

Temperature, degrees	740 mm	750 mm	760 mm	770 mm	780 mm
15	1.81	1.83	1.86	1.88	1.91
16	1.93	1.96	1.98	2.01	2.03
17	2.05	2.08	2.10	2.13	2.16
18	2.17	2.20	2.23	2.26	2.29
19	2.29	2.32	2.35	2.38	2.41
20	2.41	2.44	2.47	2.51	2.54
21	2.53	2.56	2.60	2.63	2.67
22	2.65	2.69	2.72	2.76	2.79
23	2.77	2.81	2.84	2.88	2.92
24	2.89	2.93	2.97	3.01	3.05
25	3.01	3.05	3.09	3.13	3.17
26	3.13	3.17	3.21	3.26	3.30
27	3.25	3.29	3.34	3.38	3.42
28	3.37	3.41	3.46	3.51	3.55
29	3.49	3.54	3.58	3.63	3.68
30	3.61	3.66	3.71	3.75	3.80

Vapor Pressure of Water

t, degrees	p, millimeters	t, degrees	p, millimeters	t, degrees	p, millimeters	t, degrees	p, millimeters
0	4.6	26	25.2	40	55.3	90	526.0
5	6.5	27	26.8	45	71.9	95	634.0
10	9.2	28	28.3	50	92.5	96	657.7
15	12.8	29	30.1	55	118.1	97	682.1
20	17.5	30	31.8	60	149.5	98	707.3
21	18.7	31	33.7	65	187.6	99	733.2
22	19.8	32	35.7	70	233.8	100	760.0
23	21.0	33	37.7	75	289.3	101	787.6
24	22.4	34	39.9	80	355.5	102	816.0
25	23.8	35	42.2	85	433.8	103	845.3

Density of Water

Degrees	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	0.999841	847	854	860	866	872	878	884	889	895
1	0.999900	905	909	914	918	923	927	930	934	938
2	0.999941	944	947	950	953	955	958	960	962	964
3	0.999965	967	968	969	970	971	972	972	973	973
4	0.999973	973	973	972	972	972	970	969	968	966
5	0.999965	963	961	959	957	955	952	950	947	944
6	0.999941	938	935	931	927	924	920	916	911	907
7	0.999902	898	893	888	883	877	872	866	861	855
8	0.999849	843	837	830	824	817	810	803	796	789
9	0.999781	774	766	758	751	742	734	726	717	709
10	0.999700	691	682	673	664	654	645	635	625	615
11	0.999605	595	585	574	564	553	542	531	520	509
12	0.999498	486	475	463	451	439	427	415	402	390
13	0.999377	364	352	339	326	312	299	285	272	258
14	0.999244	230	216	202	188	173	159	144	129	114
15	0.999099	084	069	054	038	023	007	*991	*975	*959
16	0.998943	926	910	893	877	860	843	826	809	792
17	0.998774	757	739	722	704	686	668	650	632	613
18	0.998595	576	558	539	520	501	482	463	444	424
19	0.998405	385	365	345	325	305	285	265	244	224
20	0.998203	183	162	141	120	099	078	056	035	013
21	0.997992	970	948	926	904	882	860	837	815	792
22	0.997770	747	724	701	678	655	632	608	585	561
23	0.997538	514	490	466	442	418	394	369	345	320
24	0.997296	271	246	221	196	171	146	120	095	069
25	0.997044	018	*992	*967	*941	*914	*888	*862	*836	*809
26	0.996783	756	729	703	676	649	621	594	567	540
27	0.996512	485	457	429	401	373	345	317	289	261
28	0.996232	204	175	147	118	089	060	031	002	*973
29	0.995944	914	885	855	826	796	766	736	706	676
30	0.995646	616	586	555	525	494	464	433	402	371

* Figures designated with an asterisk apply to the number given in the next lower row.

Methods of Expressing Concentrations

The concentration of solution may be expressed in any of the following ways:

a. Percentage by weight.   (Grams solute ÷ grams solute + grams solvent.)

b. Moles per 1,000 ml of solution.   ("Molar" = 1 mole in 1,000 ml of solution.)

c. Moles per 1,000 g of solvent.   ("Molal" = 1 mole in 1,000 g solvent.)

d. Mole fraction.   (Moles solute ÷ moles solute + moles solvent.)

For technical work, (*a*) is used; (*b*) is very convenient in volumetric analysis; (*c*) is used in certain theoretical work, because the temperature variable is eliminated; and (*d*) is extensively used in theoretical work involving physical properties of solutions.

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